VERIFIED SYNTHESES OF ZEOLITIC MATERIALS

Second Revised Edition

Harry Robson, Editor
Karl Petter Lillerud, XRD patterns

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Preface to the second edition

The first edition of Verified Syntheses of Zeolitic Materials was published as Volume 22, Nos. 4-6 of Microporous and Mesoporous Materials (30 June 1998). Distribution was limited to subscribers to the Journal. The second edition is planned for publication in mid 2001 in time for distribution at IZC-13 (Montpellier, July 2001).

The format for the second edition is largely unchanged from the first. The intended audience is still the applications researcher, reasonably skilled in the art, who wants a particular phase enough to attempt its synthesis in the laboratory. In practical terms, this means approximately first year graduate students. With the exception of organic templating agents, zeolite synthesis does not require elaborate equipment or expensive reagents. As evidenced by the contributors list, many investigators in many different countries have been active in the synthesis field.

The current edition has reprinted all the recipes from the first edition plus 24 new recipes. The introductory articles on basic skills in zeolite synthesis includes the articles from the first edition (some with substantial revisions) plus five new articles. The XRD patterns have been recorded using different instrument settings from those in the first edition and are intended to conform to typical X-ray diffraction practice. In most cases, only the XRD pattern for the product as synthesized is printed here. The exceptions are those phases which show marked changes in the XRD pattern upon calcination.

Zeolite synthesis is an active field of research. As long as this continues, new phases will be discovered and new techniques for preparing existing phases will appear. The IZA Synthesis Commission hopes to continue and enlarge this collection to include all phases of interest to the zeolite research community.

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of the

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Previous IZA Special Publications

- W. J. Mortier, *Compilation of Extra Framework Sites in Zeolites* (1982)
- W. M. Meier, D. H. Olson and Ch. Baerlocher, *Atlas of Zeolite Structure Types*, 4th edition (1996)
- M. M. J. Treacy, J. B. Higgins and R. von Ballmoos, *Collection of Simulated XRD Powder Patterns for Zeolites*, 3rd edition (1996)
- H. E. Robson and K. P. Lillerud, *Verified Syntheses of Zeolitic Materials*, 1st edition (1998)

Introduction and explanatory notes

Accounts of synthesis experiments reported in the literature are nearly always cryptic leaving the reader who wants to repeat the experiment many choices of reagents and procedures. In most cases, there are multiple experiments producing similar products without a clear indication of which one the author(s) prefer. Characterizations of the products are often inadequate for an unambiguous choice for a new application.

Experts in the art of zeolite synthesis have learned to accept these ambiguities and persevere through early failures to reproduce the desired product in most, not all, cases. The neophyte may be less diligent; and early failures may be the end of the critical experiment leading to a new application. The IZA Synthesis Commission in preparing this volume seeks to improve the success ratio for synthesis experiments by encouraging the contributors to better define their experiments and adequately characterize their products.

The Organizing Committee, which preceded the Synthesis Commission, surveyed experts in the synthesis area and published an outline covering the essential points for reporting a zeolite synthesis [1]. The format for the recipes in this volume follows this outline. The table form is intended to assist the reader by placing the information in the same relative positions for all recipes. The table form supposes that all synthesis experiments follow the general sequence: batch preparation, crystallization, product recovery, and characterization.

1. Framework Type Codes

The three-letter codes (top line - far left) are arranged in alphabetical order as in the Atlas of Zeolite Structure Types [2]. They define the topography, but not the composition of the resulting phase. Unlike the Atlas, which has one entry for each code, this volume may contain multiple entries for a single code with differing Si/Al ratio products, products with differing T-atoms, or products of essentially the same composition produced by different synthesis procedures.

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2. Product Name

The product name (top line - center) is the name by which the product is usually referred to in the literature. There may be several products of similar composition but different names. A more complete list of these names can be found in the Atlas section "Isotypic Framework Structures" for that framework type code. The choice among competing names has been left to the contributing author in most cases. The number of framework type codes is large but limited; the number of products or recipes is unlimited. As long as zeolite synthesis is an active field of research, there should be new recipes for later editions of this volume.

3. T-atom Composition

T-atom composition (top line - far right) refers to the elements which occupy tetrahedral positions in the framework and their relative numerical abundance (basis:100 T-atoms). The values are based on the elemental analysis of the product of the recipe as given in Product Characterization. In most cases, values are rounded to integer values except where a minor T-component has particular significance.

4. Contributed by

The name(s) indicate the person or persons who actually prepared the entry and is intended to identify the one most likely to respond to communications regarding the recipe. The entries are not intended for full scientific recognition for the research which produced the recipes; in most cases, recognition has already occurred elsewhere in the literature. Authors are identified by name only; academic titles and institutional affiliation are given in the contributors section. Single contributors are listed except where the authors expressly stated co-authorship.

5. Verified by

Verifiers are those independent investigators who have reproduced the synthesis experiment and obtained a satisfactory product by their own evaluation. Again, only names are given here; for institutional affiliation, see the contributors list. Only those verifiers who responded affirmatively are listed here. Negative responders, those who replicated the experiment but obtained a product other than the desired phase, are acknowledged in the contributors section. These reports, both positive and negative, are part of the record of the recipe and are available on request. In many cases, the responses of verifiers have prompted changes in the recipes.

6. Type Material

Type material refers to contents of the unit cell as indicated by the elemental analysis. In most cases, the product has been washed and dried but not calcined. Thus the template is often a component of the product composition. Water contents of the products are not consistent; only in some cases has the synthesis product been equilibrated under controlled humidity.

7. Method

Method cites the literature report on which the recipe is based, usually the author's report but sometimes an earlier, more general reference. Patent references have been avoided unless they are specific. It is the intention of this volume that the reader be directed to the single recipe which gives the best chance of immediate success in the synthesis.

8. Batch Composition

Batch composition refers to the product of batch preparation stated in ratios of oxides, template molecules and neutralization products. The basis is usually a single formula weight of Al_2O_3 or another trivalent oxide; occasionally the base is SiO_2 or P_2O_5.

9. Source Materials

Source materials are those actual materials used to prepare the batch along with their purity and supplier. Generally the source materials are stated in the order in which they are used in preparing the batch. The authors have been encouraged to be specific as to the suppliers because many failures to replicate have been traced to the change of supplier for a source material, particularly in the case of silica or alumina. In most cases, the balance of the composition of the component is assumed to be H_2O and should be included in calculating batch composition.

10. Batch Preparation

Batch preparation refers to actual quantities of materials plus the preparation steps used to prepare material for the crystallization step. The estimate of product yield is intended for the reader's convenience. For each step, the materials added **and the order of addition** are indicated within the brackets. Order of addition has been found to be critical in some cases. Instructions for completing the step follow the brackets. Combination at room temperature is contemplated unless otherwise stated. Completion of the batch preparation in a matter of minutes or of hours is expected unless delay is specifically required.

11. Crystallization

Crystallization refers to the experimental conditions and temperature profile which converts the finished batch to a product slurry of zeolite crystals in a "mother liquor." The containing vessel is assumed to be inert except in special cases. Accidental seeding by residues of earlier experiments has been shown to be a problem. If autoclaves or their liners are reused, they

should be carefully cleaned. Rapid heat-up to the crystallization temperature is contemplated; rarely is the heat-up time a significant portion of the total treatment. Temperature fluctuations during treatment are to be expected.

Aging or incubation of the finished batch at ambient or some intermediate temperature is part of some treatments. Time / temperature tradeoffs are described in the literature; the intention here is to give the author's best guess as to the optimum treatment. Monitoring the progress of crystallization can be instructive, but it is difficult in closed autoclaves at temperatures above 100°C. Rather than sample at temperature or cool, sample, and reheat, the usual approach is to divide the batch into several vessels and treat the aliquots for progressively longer times.

Static treatments or only modest or intermittent agitation is the usual case. Continuous agitation may be required for specific preparations.

12. Product Recovery

Product recovery refers to the procedure for separating the desired product from the by-products of the crystallization process. Most zeolite products are micron-sized crystals which are easily filtered while the "mother liquor" is a solution of excess alkali silicate, excess template, etc. Very fine product crystals may require centrifugation for good product recovery. For alkaline synthesis, the pH drops as the washing proceeds; pH = 10 for the final wash is usually sufficient. For fluoride synthesis or $AlPO_4$-type materials, other criteria for adequate washing are required.

Although most zeolite products are water stable, prolonged washing can produce subtle changes in their composition. Hydrolysis may replace cations with H_3O^+; salt or template inclusions may be reduced or eliminated. Some investigators prefer to wash with dilute NaOH rather than pure water. In general, washing conditions must be considered part of the synthesis.

Drying usually is accomplished in a laboratory oven at ~110°C. It is good technique to equilibrate the dried sample at a constant 50% humidity to make it stable to handling in laboratory air. Yield here is expressed as percent of theoretical yield based on the limiting component (usually Al_2O_3 or SiO_2). In the literature, yield is sometimes expressed as percent by weight based on the finished crystallization batch.

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12.1 Flocculation [3]

Sometimes flocculation, a method of agglomerating fine particles to filterable size, is advantageous. An example of an organic flocculant is a detergent-type molecule, which adsorbs with the hydrophilic end on the hydrophilic zeolite particle surface, with the hydrophobic end extending into the aqueous medium. The thus generated hydrophobic particles coagulate to form flocs or flocks, which can be filtered and washed on the filter with water.

Before applying such an organic flocculant, the alkalinity of the crystallized reaction mixture needs to be reduced. The application of an electrolyte, such as NaCl, as a flocculant, however, has the disadvantage that colloidal silica present in the mother liquor is coagulated as well, so that the crystallinity of, for example, zeolite alpha, will be ≤90%. If this is acceptable, NaCl is added with mild stirring (magnet bar) until, after turning off the stirrer, flocs become visible, first where the meniscus meets the glass. The flocculated product will settle, and the supernatant liquid can be decanted. The sediment may be filtered, but washing with water causes the flocs to disintegrate, and the crystallites will pass the filter again. Washing, however is not necessary. Instead, the filter cake is reslurried, and now an organic flocculant, such as Betz No. 1192, which is added in small portions of a 0.2% solution, until complete flocculation is observed, can be applied. The thus flocculated product can be filtered and washed with water.

If coagulation of the colloidal silica is to be avoided, the strongly diluted crystallized reaction mixture can be left undisturbed for settling, if necessary, for as long as a few days, or centrifuged. The supernatant solution is cautiously decanted from the sediment. If complete settling is not achieved, the small amount of solids left in suspension may be sacrificed. The sediment is then reslurried and flocculated with an organic flocculant, such as Betz No. 1192, filtered and washed, as described above.

13. Product Characterization

Product characterization identifies the crystalline product and compares its properties to those of known standards. For this volume, basic characterizations are the X-ray diffraction pattern, elemental analysis and crystal size and habit from SEM. For particular applications, several other characterizations might be desired, such as sorptive capacity, ion exchange properties, thermal analysis, nuclear magnetic resonance, etc. Not many authors report their products in such detail, and in some cases it is difficult to obtain data reproducible in another laboratory. Secondary characterization, when provided, are reported in the Notes section.

14. XRD

XRD refers to the principal phase as identified by comparison of its x-ray diffraction pattern with those in the literature. Unit cell parameters are usually given. When competing crystalline phases have been identified from extraneous lines, they are indicated plus an estimate of amorphous material from the background intensity.

A reference pattern for the product in the "as synthesized" is attached. In some cases a second pattern of the calcined product is provided. Some of the calcined materials, particularly $AlPO_4$ and $GaPO_4$, are moisture-sensitive. For other cases the calcined material is virtually identical in the XRD pattern to the as-synthesized sample. In such cases no XRD trace of the calcined product is given. A separate article describes the instrument conditions for recording the XRD patterns.

15. Elemental Analysis

Elemental analysis gives ratios of metal cations present usually expressed as the ratios of their oxides. The editor prefers the direct analytical result (weight percent of the element or its oxide based on the dry sample). Most authors give ratios of the oxides based on one formula weight of Al_2O_3 or SiO_2. In most cases, these were determined by inductively coupled plasma emission spectroscopy. In some cases, the content of water or template molecules in the product as indicated by thermal analysis is also included.

16. Crystal Size and Habit

Crystal size is an estimate of the crystallite size and/or the aggregate particle size. Habit is a qualitative description of the sample as observed in the SEM.

17. References

References indicate the primary literature report on which the recipe is based plus selected general references recommended by the author. This list is intentionally limited and is intended to start the user's search of the literature, not complete it.

18. Notes

The notes give additional instructions or information which the author believes helpful to the reader but which do not fit into the recipe format. The additional instructions are intended to substitute for a private conversation with the author before the reader/user begins the synthesis experiment. It is potentially the most valuable part of the contribution.

References

[1] H. Robson, Zeolites, 13 (1993) 399
[2] W. M. Meier, D. H. Olson, Ch. Baerlocher, Zeolites, 17 (1996) 1
[3] G. Kühl, personal correspondence

Conditions for recording of XRD patterns reported in this book

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The X-ray diffraction (XRD) patterns were recorded with a SIEMENS D5000 diffractometer. The diffractometer was equipped with a Ge-focusing primary monochromator giving Cu-Kα1 radiation (λ = 1.5406 Å), a BROWN 70 mm linear position sensitive detector (PSD) and a 40 position sample changer. The PSD is operated with 8° opening. A variable entrance slit giving a constant 6 x 12 mm exposed area is used.

The reported intensity distribution is for fixed slit geometry. The diffraction patterns are recorded with variable slit, but presented with at the intensity distribution recalculated to simulate fixed slit mode. The intensity scale (ordinant) for all patterns is K-Counts/second.

For comparison with measured diffraction patterns is it important to note that routine measurements are often performed with a slit that will expose more than the sample area at low angle. The observed intensities at low angle will therefore be too small compared with these reference patterns and calculated patterns.

In this version of the collection all patterns are scaled to the same absolute intensity. The diffraction patterns are presented in the as measured condition without any background subtraction or smoothing. Some samples contain elements that give raised fluorescence, like Fe and Co. No filter or secondary monochromator has been used to remove this radiation.

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Verified Syntheses of Zeolitic Materials. H. Robson, editor

Source materials for zeolite synthesis

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1. Introduction

The chemistry of zeolite synthesis is subject to perturbations caused by impurities present in the source materials. Such contaminants may remain insoluble during the crystallization and cause undesired species to nucleate. They may be soluble and result in formation of different silicate or metallosilicate species in solution, or they may cause an insoluble silicate species to precipitate. Therefore, it is desirable to apply pure chemicals as starting materials. Depending on the zeolite to be synthesized and the application intended for the product, less pure source materials are frequently employed, in order to reduce the cost. If the materials are not pure, they may vary from batch to batch and from different suppliers. It is of utmost importance to know the source materials for zeolite synthesis, and technical grade materials need to be assayed and analyzed for impurities. A few frequently used chemicals are discussed below.

2. Water Content

Clearly, when commercially available solutions of chemicals are employed, such as aqueous NaOH, H_2F_2, or silicate, the water content of the solution has to be taken into account when the composition of the reaction mixture is established. Most other source materials contain more or less water, while the water content of fume silica may be only 3 wt.%, that of aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$, is about 43 wt.%. Moreover, aluminum nitrate is deliquescent, and the water content will change once the jar has been opened and the chemical exposed to moist air. On the other hand, aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$ (48.6 wt.% H_2O), weathers by losing water upon exposure to the atmosphere. Technical grade aluminum sulfate usually contains about 14 H_2O.

Since the composition of a reaction mixture is given as ratio of oxides, any hydroxides employed are to be considered as oxides plus water, for example, $NaOH = 1/2Na_2O + 1/2H_2O$ (22.5 wt.% H_2O). Additionally, a small percentage of free water may be present, for example, sodium hydroxide pellets may contain about 97 or 98% NaOH. Similarly, an 85% H_3PO_4 contains 61.6 wt.% P_2O_5 and 38.4 wt.% H_2O. The water content of source materials may or may not constitute an important fraction of the total water content, and it is recommended that the water contained in these chemicals always be considered when the amount of water to be added in the preparation of the reaction mixture is calculated.

3. Sources of Aluminum

Some aluminum sources have been mentioned above. A disadvantage of using salts is that, after pH adjustment or addition of alkali silicate solutions, alkali salts are formed which have a strong electrolytic effect on gel formation. For example, such salts may cause sodalite to be crystallized instead of zeolite A type materials. For this reason, it is advantageous, particularly for reaction mixtures of low SiO_2/Al_2O_3 ratios, to introduce aluminum in the anionic form, that is, as sodium aluminate.

Sodium aluminate is subject to formation of aluminum oxide hydrates upon exposure to atmospheric carbon dioxide or just upon storage. It is not a widely used chemical, and, when obtained from a chemical supplier, is frequently aged to an extent that makes it unsuitable for zeolite synthesis. Sodium aluminate should dissolve completely with stirring in water at ambient temperature within a few minutes. If it does not, the precipitate or cloudiness usually can not be

dissolved by adding small quantities of alkali hydroxide, and the chemical is not suitable. Fresh sodium aluminate can be obtained in a technical form in larger quantities. such as 50-lb. bags. It is advisable to transfer the chemical with as little exposure to moisture and CO_2 as possible into small jars which should be sealed tightly and stored at or below room temperature. The composition of such technical sodium aluminate varies widely with Na/Al ratios from near 1.0 to 1.2 or higher so that a reliable assay is required. A small iron content manifests itself by the brownish discoloration of the otherwise clear sodium aluminate solution. This iron hydroxide can be removed by filtration or, for less critical preparations, just ignored.

In preparations containing phosphate, aluminum phosphate, $AlPO_4 \cdot 2H_2O$, is a viable alternative as it dissolves completely in alkaline phosphate or hydroxide solutions upon mild heating with stirring.

4. Silica Sources

A widely used silica source is aqueous sodium silicate, such as waterglass from PQ Corporation, Philadelphia, PA, USA. The PQ N-Brand product contains about 8.9 wt.% Na_2O and 28.7 wt.% SiO_2. It usually is slightly cloudy, and it is recommended that filtered N-Brand be purchased. The precipitate can also be filtered off in the laboratory, but the vacuum filtration is slow and the filtrate has a reduced water content and needs to be reassayed. A small contamination with aluminum usually prevents zeolites with SiO_2/Al_2O_3 ratios above ~600 to be crystallized.

When a lower aluminum content in the product is desired, colloidal silica sol, such as Ludox from E. I. DuPont de Nemours, Wilmington, DE, USA, can be used. This material is available in concentrations of 30 and 40 wt.% SiO_2 with different stabilizers employed. Without added aluminum, SiO_2/Al_2O_3 ratios in the range of 3000 to about 3500 can be obtained.

Zeolites of still lower aluminum content can be prepared with fume silica as the silica source. Such materials are on the market as Cab-O-Sil (Cabot) or Aerosil (Degussa). The water content of fume silica is very low, ~3 wt.%. Products obtained when using fume silica as the silica source, without adding an alumina source, have SiO_2/Al_2O_3 ratios above 20,000.

Precipitated silica is available in different qualities. Hi-Sil (PPG Industries, Pittsburgh, PA, USA) contains about 90 wt.% of SiO_2 as well as ~1 wt.% of NaCl (it is recommended that the percentage of SiO_2 be determined; alternatively, the ash content minus 1% NaCl should approximate the SiO_2 content). The aluminum contamination prevents zeolites with SiO_2/Al_2O_3 ratios above ~220. A somewhat purer material is Ultrasil (Degussa). The particle size of precipitated silica may need to be considered. Whereas finely divided fume silica may yield a thick paste of a reaction mixture, which is difficult to homogenize, a large-size precipitated silica, for example, Ultrasil VN3SP, may react too slowly to provide the desired aluminosilicate precursors in solution.

Tetramethyl- and tetraethylorthosilicate are available in high purity and yield the highest SiO_2/Al_2O_3 ratios. Any noticeable aluminum contamination is likely brought in from other sources. The compounds are usually hydrolyzed, for example, in a stainless-steel beaker, prior to incorporation in a reaction mixture. It is recommended that the alcohol generated be removed by heating, although its effect on the crystallization of high-silica materials is generally slight.

In order to prevent contamination, plastic containers such as polypropylene or Teflon, are recommended for the preparation of all solutions, for the reaction mixture, and for the crystallization. Glass vessels should be avoided, as glass participates in the reaction, and silica, alumina, and boron are known to be leached out of glass. For example, the catalytic activity of a borosilicate or a ferrosilicate may be influenced by contamination with traces of aluminum. When pressure vessels are used for the crystallization, removable Teflon or stainless-steel liners are recommended. The reaction vessels should be thoroughly cleaned prior to use by heating with aqueous sodium hydroxide, if seeding is to be avoided. Teflon may also be cleaned with hydrofluoric acid.

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Verified Syntheses of Zeolitic Materials. H. Robson, editor

Nucleation, growth, and seeding in zeolite synthesis

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1. Zeolite Crystallization

Crystallization from solution generally occurs via the sequential steps of nucleation of the phase, or phases, dictated by the composition of the solution, followed by growth of the nuclei to larger sizes by incorporation of material from the solution. Nucleation and crystal growth rates typically are governed by a driving force related to the supersaturation.

Molecular sieve zeolites usually are precipitated from aluminosilicate solutions in basic media, frequently at elevated temperatures and autogenous pressures. Most commercially interesting syntheses are preceded by the formation of an amorphous gel phase which dissolves to replace reagents consumed from the solution by crystal growth. Some experimental systems which are "crystal clear" have been developed that permit certain *in situ* analytical techniques to be used to study the crystallization process.

In hydrothermal zeolite systems it is more difficult to identify a "supersaturation," because of the myriad species present in the aluminosilicate solution, because of the role of structure directing agents in some cases, and because the relative concentrations of these in a batch system change as the crystallization proceeds. For these reasons, the issue of defining the precise driving force for zeolite nucleation and crystal growth has yet to be accomplished with any degree of certainty. However, recent progress has been reported in defining solubility products and crystallization diagrams for zeolites NaA and NaX, and further progress can be expected using the approach developed there. [1]

2. Zeolite Nucleation

It is expected that the crystallization processes occurring in hydrothermal zeolite precipitation are similar to those which are known to occur in simpler inorganic or organic crystallization systems. That being the case, one should note that nucleation mechanisms in liquid-solid systems have been divided into several categories, most notably [2,3]:

1. Primary Nucleation
   - Homogeneous
   - Heterogeneous
2. Secondary Nucleation
   - Initial breeding
   - Contact
   - Shear
   - Fracture
   - Attrition
   - Needle

Chapter 5 of the text by Randolph and Larson provides excellent background on these mechanisms. [2] The primary references contained in their bibliography also are quite informative.

Primary nucleation is characterized as being driven by the solution itself, either strictly within the solution, as in homogeneous nucleation, or catalyzed by extraneous material in the solution, as in heterogeneous nucleation. Certainly with the presence of amorphous gel in most zeolite synthesis systems, one might anticipate that heterogeneous nucleation on gel surfaces might be important. This has yet to be demonstrated unequivocally.

Secondary nucleation is catalyzed by the presence of parent crystals of the same phase, and occurs with a lower activation energy than primary nucleation. The parent crystals might be added as seed crystals at the beginning of a synthesis, or grown in the original unseeded system. Initial breeding results from the addition of seeds which will be discussed below. The other secondary nucleation mechanisms could stem from added seed crystals or crystals grown *in situ*.

For example, Culfaz and Sand reported that new mordenite crystals appeared to grow from seed crystal surfaces and break off acicular pieces, resulting in nuclei formation as the dendritic pieces grew to macroscopic sizes. [4]

The mechanisms involving secondary nucleation induced by fluid shear, contact (or collision) breeding, and fracture all require sufficient fluid motion to cause physical damage to the parent crystals, and thereby promote formation and release of secondary nuclei from the parent crystal surface. In many zeolite systems, there is no induced fluid motion, as by stirring, and crystal settling is generally viewed as insufficient to cause secondary nucleation. A review of the evidence suggesting that agitation-induced secondary nucleation is not important in zeolite systems was published recently. [5] More recently, an interesting study by Falamaki, et al, has suggested that severe agitation during synthesis of ZSM-5 was not sufficient to either promote nucleation or to break ZSM-5 crystals. [6]

The numerous works by Subotic, et al., and references contained therein, have pointed to the possibility that nuclei form within the amorphous gel matrix, and are released to become viable growing crystals as the gel phase dissolves. [7] This mechanism is still under review, and yet may be plausible given the new evidence that nanometer-sized particulates (or nanoparticles) have been observed in clear solution synthesis mixtures, and may be the origin of nuclei. [8] It has not yet been determined how or when these nanoparticles form, although recent progress has been made in determining that they form almost instantaneously in the MFI synthesis system. [9]

3. Crystal Growth

Most crystallization processes involve assimilation of material from solution via a growth process which can be described by the relation [2,3]:

$$\frac{dL}{dt} = G = Ks^a$$

Where a is an exponent expressing the dependence of the linear crystal growth rate, G, on the supersaturation, s, and K is a temperature-dependent rate constant. The value of *a* will be 1.0 for diffusional transport limitations to a planar crystal surface, and between 1-2 for most surface reaction limited growth processes. [2,3] Schoeman, et al. have analyzed the growth rate behavior for Silicalite in clear solutions using a chronomal analysis and concluded that its growth rate is limited by a first-order surface reaction with an activation energy of 42 kJ/mol. [10] A recent summary of several reports of activation energies for zeolite crystal growth showed values to be in the range of 43-96 kJ/mol, magnitudes which certainly suggest surface kinetics limited growth rather than diffusional limitations. [11]

A debate has arisen in the literature recently regarding what species actually add to the crystal surface to promote growth and whether an agglomeration mechanism plays a role in zeolite crystal growth. Schoeman used the DLVO theory for colloidal stability to predict that nanoparticle agglomeration would not be possible in a Silicalite synthesis solution. [12] He concluded that zeolite crystal growth was supported by addition of low molecular weight species, most likely the monomer. He also concluded that the nanoparticles, observed by several research groups, would be predicted to be stable in Silicalite synthesis solutions. However, Kirschhock, et al. extended Schoeman's work to show that growth by agglomeration of nanoparticles with crystal surfaces was possible. [13] Specifically, they noted that the nanoparticles should come to rest at about 7 Å from the crystal surface in an energy well, and have ample time to orient and chemically bond to the surface. More recently, Nikolakis, et al. analyzed Silicalite crystal growth and the energetics of nanoparticle-crystal interactions using atomic force microscopy. [14] They also extended the DLVO theory and concluded that zeolite crystal growth by nanoparticle addition was possible, even though their total potential energy curves showed no energy wells or negative values at distances greater than a fraction of an angstrom.

Nothing definitive can be said about this debate at this time. Thus, growth by addition of monomers, low molecular weight species, or nanoparticles cannot be ruled out. However, growth is suggested by the magnitudes of activation energies to be limited by surface reaction kinetics rather than diffusion from the bulk liquid to the crystal surface, and the nanoparticles would be expected to diffuse rather slowly, potentially at rate-limiting rates, due to their very large molecular weights. These observations might lead one to suspect that growth should be by addition

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of low molecular weight species or monomers.

4. Seeding

Adding seed crystals to a crystallization system has typically resulted in increased "crystallization" rates. The enhanced rate might be due to simply increasing the rate at which solute is integrated into the solid phase from solution due to the increased available surface area, but also might be the result of enhanced nucleation of new crystals. Understanding the precise role of seed crystals is an area of ongoing investigation.

The secondary nucleation mechanism referred to as initial breeding results from microcrystalline dust being washed off of seed crystal surfaces in a new synthesis batch, and has been reported in zeolite systems. [15] These microcrystalline fragments grow to observable sizes, and result in greatly enhanced "crystallization" rates due to the significantly increased crystal surface area compared to the unseeded system. Consequently, it is to be expected that addition of seed crystals to a synthesis system will introduce sub-micron sized crystallites into the system which will serve as nuclei.

Finally, it is worth noting that a recent study of initial bred nuclei using a clear synthesis solution [16] suggested that the initial bred nuclei themselves may be the same nanoparticles observed by Schoeman [8], Kirschhock, et al. [9], and independently elsewhere. [17]. That is, the same particulates which appear to catalyze zeolite nucleation in unseeded systems may remain in sufficient number to catalyze nucleation in seeded systems, since they are inherently present with the seed crystal sample, and may be impossible to eliminate by typical filtration techniques.

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Verified Syntheses of Zeolitic Materials. H. Robson, editor

Synthesis of high-silica zeolites and phosphate-based materials in the presence of fluoride

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1. Introduction

The most common mineralizer for silica-based zeolites is the hydroxide ion OH^-. The alkaline pH is generally adjusted by addition of an inorganic base or an organic base, especially when an organic species is used as a template. The replacement of the hydroxide anions by fluoride anions as mineralizers makes it possible to obtain zeolites even in slightly acidic media (pH ~ 5). At such pH values the solubility of silica, for example, increases significantly in the presence of fluoride because of the formation of hexafluorosilicate SiF_6^{2-} species. Such species were observed in particular in the mother liquor of fluoride Silicalite-1 by ^{19}F and ^{29}Si liquid NMR. It can be assumed that the hydrolysis of fluorosilicate anions yields polycondensable hydroxylated species whose condensation leads to the crystalline material. In the synthesis of Borosilicalite-1 the presence of the hydroxyfluoroborate anions BF_3OH^- and $BF_2(OH)_2^-$ in addition to BF_4^- and SiF_6^{2-} was indeed evidenced by ^{19}F NMR [1].

2. Synthesis of silica-based zeolites - Usual synthesis conditions with fluoride

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Typically the synthesis mixture is prepared by adding a silica source (such as fume silica, colloidal, precipitated silica), a source of framework elements if necessary (for example, B, Al, Fe, Ga, Ti), an organic species and a fluoride source. The temperatures of crystallization are similar to those used in the synthesis without F^- but the crystallization time is generally longer.

The crystals are usually of good quality and the size generally exceeds the values obtained in alkaline type synthesis.

When the crystallization is carried out in the presence of an organic cation, as in the case of silica-rich zeolites, fluoride is generally occluded in the pores of the solid as a compensating negative charge, in addition to the negative framework charge, of the organic cations. Fluoride is essentially completely removed on calcination.

The most common and preferred fluoride sources are NH_4F, NH_4HF_2 or HF. Fluoride may also be combined with the source of framework elements such as in $(NH_4)_2SiF_6$ or $AlF_3 \cdot H_2O$, and be released on hydrolysis. The calcination of the as-synthesized material then leads directly to the H form of the zeolite. However, in the case of aluminum-rich starting gels, the sparingly soluble salts NH_4AlF_4 and $(NH_4)_3AlF_6$ may be present in the as synthesized solid. They can be dissolved by washing with an aqueous alkaline dimethylamine solution.

Most of the syntheses employing the fluoride route have been carried out in aqueous medium. However, an essentially non-aqueous fluoride route has been developed for the synthesis of large crystals in the mm range using HF-pyridine or HF-alkylamines as mineralizers [2].

3. Synthesis of phosphate-based materials - Usual synthesis conditions with fluoride

In contrast to the alkaline pH values in the conventional synthesis of silica-based zeolites, the usual pH of the reaction mixture for the synthesis of phosphate-based materials such as aluminophosphates and gallophosphates is slightly acidic to slightly alkaline (typically, starting pH = 3-10). Therefore the pH conditions for the synthesis of phosphate-based materials in the

presence of fluoride are close to those that would be used in its absence.

Nevertheless, various beneficial effects are observed in the presence of fluoride. The crystallization times are generally shorter and the crystals usually larger and well formed. Thus, in the synthesis of the CHA-type materials SAPO-34 and CoAPSO-34, it was observed that, when F^- was present, the induction time was smaller (divided by about 3), but the rate of crystal growth was smaller than when it was absent [3]. It was assumed that the presence of fluoride favors the fast production of fewer nuclei, after which crystal growth consumes preferentially but slowly the precursors. The stability of the fluorocomplexes must not be so high that further reaction involving them is inhibited.

Another beneficial effect of the presence of fluoride is the production of a number of phases which do not form in a fluoride-free medium, thus showing a structure-directing role of the fluoride ion. For such phases, fluoride is generally part of the framework bonded to Al or Ga atoms as terminal or bridging species, or even trapped in double-four-ring units.

The preferred fluoride source is HF, the pH being adjusted by addition of an organic base. The presence of NH_4^+ or Na^+ cations is undesired in that case since ammonium or sodium aluminophosphates may be produced, for example $AlPO_4$-15 $NH_4Al_2OH(PO_4)_2 . 2\ H_2O$, may be produced. On calcination fluoride is removed together with the organic template.

For more information the reader is referred to the article entitled "The Opportunities of the Fluoride Route in the Synthesis of Microporous Materials" by Kessler, Patarin and Schott-Darie [4].

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Verified Syntheses of Zeolitic Materials. H. Robson, editor

Templating in molecular sieve synthesis

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Zeolite crystallization is a very complex phenomena that cannot be adequately described by the classical variables of reactant composition, temperature, and pressure. Crystallization also involves polymerization-depolymerization, solution-precipitation, nucleation-crystallization, and other complex phenomena encountered in aqueous colloidal dispersions.

In the early descriptions of molecular sieve synthesis, the species that formed the oxide framework (such as silicate, aluminate) were distinguished from extraframework species, such as exchangeable cations (Na^+, K^+) and water. In some cases the "exchangeable" cations were not completely exchangeable without significant structural damage (such as K^+ in OFF). Nevertheless, the cations played an obvious role in the charge compensation of the alumina tetrahedra in the product. Less obviously, the frequent association of certain alkali cations with the presence of smaller cage structures led to the concept of a mechanistic role that was designated "templating." Templates were cationic species added to synthesis media to aid/guide in the polymerization/organization of the anionic building blocks that form the framework.

In one of the first broad studies of zeolite crystallization in the presence of mixed alkali-organic bases, Aiello and Barrer explained the observed structure specificity of the mixed cations by introducing the concept of templating of the different cage structures by the larger organic and smaller alkali cations. [1] In particular, the quaternary organic tetramethylammonium (TMA) appeared to play an important role in the formation of the OFF and MAZ structures, since these structures were not observed in its absence. The authors suggested that the TMA helped form the aluminosilicate precursor of the gmelinite cage building unit that was common to both structures through a templating action. In a subsequent study of the role of multiple cations, H. Khatami postulated that in the synthesis of zeolites from systems containing ternary, quaternary, or higher numbers of cations, "the zeolite framework structure is determined by one or at most two cations depending on their type and size. Additional cations, should they be included in the lattice, affect the zeolite properties but have minimal or no influence on the structure topology." [2]

In 1973 Flanigen reviewed the concepts governing zeolite crystallization and observed that cations play "a prominent structure-directing role in zeolite crystallization. The unique structural characteristics of zeolite frameworks containing polyhedral cages have led to the postulation that the cation stabilizes the formation of structural subunits which are the precursors or nucleating species in crystallization." [3,4,5] The many zeolite compositions and complex cation base systems

Table 1. Synthesis cation specificity for framework structures

Structure Type	Polyhedral Building Units	Synthesis Cations	Cation Specificity
LTA	D4R, sodal, α	Na, Na-TMA, Na-K, Na-Li	Na
FAU	D6R, sodal	Na, Na-TMA, Na-K	Na
KFI	D6R, α	Na-DDO, (Ba?)	Na-DDO
GME	D6R, gmel	Na, Na-TMA	Na
MAZ	Gmel	Na-TMA, Na-K-TMA, Na-Li-TMA	Na-TMA
OFF	D6R, gmel, canc	K-TMA, K-Na-TMA	K-TMA
ERI (with OFF)	D6R, canc (gmel)	Na-K, Ba-TMA, Na-Rb, Na-TMA Na-K-TMA, Na-Li-TMA, Na-K-BTMA	Na-K, Na-Rb, Na-TMA Ba-TMA
LTL	D6R, canc	K, K-Na, K-DDO, K-Na-TMA, Ba, Ba-TMA	K or Ba
CHA	D6R	Na, K, Na-K, Ba-K, Sr	Na, K, or Sr

D4R = double 4-ring, D6R = double 6-ring, sodal = sodalite cage, α = truncated cuboctahedron, gmel = gmelinite cage, canc = cancrinite cage.

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were compelling examples of the structure-directing role of the cation and the cation "templating" concept. In this early context "templating" and "structure-directing" were synonymous.

Table 1 shows some of the early cation/structure relationships. It is clear from this table and other data that some structures exhibit a structural cation specificity (such as LTA and FAU for Na) while others do not (such as ERI, CHA). Table 2 further delineates the relationship between building units and cations in the early zeolite structures. The formation of a specific framework type and a polyhedral building unit depends on one or at most two cation species. The cation specificity is strong for the α-cage, sodalite cage, gmelinite cage and D4R unit. It is weak for the D6R unit. In some cases the cation (hydrated or anhydrous) is observed to fit nicely into the building unit; in others, multiple cations are present.

Table 2. Synthesis cation-building unit relationship

Building Unit	Structure-types containing building unit	Cation specificity for building unit
α	LTA, KFI	Na
Sodalite	LTA, FAU	Na or TMA
Gmelinite	GME, OFF, MAZ	Na or TMA
Cancrinite	ERI, OFF, LTL	K, Ba, or Rb
D4R	LTA	Na
D6R	FAU, KFI, CHA, GME, ERI/OFF, LTL	Na, K, Sr, Ba

In 1983 Lok, et al., reviewed the role of organic molecules in molecular sieve synthesis at a time when most new structures were the result of synthesis in the presence of different quaternary ammonium cations or amines. [6] The charge distribution and the size and geometric shape of the template were invoked to explain structure direction. These authors also addressed the persistent issue of template specificity. It was already known that in some instances: 1) one template can give rise to several different structures, 2) many templates can yield the same structure, and 3) some structures require the presence of a particular template. The solution to this dilemma was the interplay of templating and "gel chemistry" where "gel chemistry" represents all the other reaction parameters governing the gel, such as oxide composition, temperature, time, reagent type, pH. In a real sense the template was a necessary but not a sufficient condition for structure formation.

As larger and more complex organic cations were employed, the resulting structures had the organic species filling not just cages, but channels (such as 1,8-diaminooctane in ZSM-48) and channel intersections (such as tetrapropyl-ammonium in MFI). The ability of quaternary ammonium polymers to influence and to direct crystallization of zeolites was described by Rollmann et al. for a series of 1,4-diazabicyclo[2.2.2]octane-based polyelectrolytes. Examples are given in which the polyelectrolytes force crystallization of the large-pore zeolite mordenite where the small-pore species analcite would otherwise have resulted. Polymeric cations prevented stacking faults in a synthetic gmelinite, faults which had hitherto restricted access to the 12-ring channels of both natural and synthetic samples of this zeolite. [7]

In addition to the more numerous and readily available quaternary ammonium cations, other classes of nitrogen-free, cationic templates have also been used successfully. Complexes of alkali cations with crown ethers have been exploited to make novel structures (such as EMT) and known structures with novel compositions (such as FAU, KFI, RHO). [8] Balkus found that a variety of stable, cationic, substituted metallocenes could also be used to template novel structures. [9,10]

More recently, there have been several reviews that address structure-direction in high-SiO_2 zeolite crystallization. The concepts of structure-directing agent (SDA) and pore filling agent have been used to describe the relationship between the relatively hydrophobic organic cations and the oxide lattice with little or no framework charge. Davis and Zones and their coworkers [11,12] have attempted to correlate the ability of an organic cation for structure-direction in zeolite synthesis with its hydrophobicity and rigidity. The hydrophobicity of a variety of SDA's was evaluated by measuring the phase transfer behavior of the iodide form from H_2O to $CHCl_3$. The

rigidity was evaluated from the number of tertiary and quaternary connectivities. SDA's with intermediate hydrophobicity were found to be most useful for high-SiO_2 molecular sieve synthesis. In terms of SDA geometry, a bulky, rigid molecule with limited conformational variability tends to template a single structure. The use of relatively flexible molecules with a minimum diameter of ~5Å gives more than one molecular sieve, depending on the gel chemistry. Zones and coworkers have designed and prepared numerous bulky, rigid templates and used them to synthesize a great variety of new high-SiO_2 molecular sieves.

Lobo, et al., have also reviewed the concepts of structure-direction in the synthesis of clathrasils and high-silica zeolites with emphasis on the energetic interactions between the organic guest and the inorganic framework. [13] The effects of size, geometry, and the chemical nature of the organic structure-directing agent on the crystalline structures that are formed were discussed beginning with clathrasils and ending with 12-ring zeolites with 3-dimensional pore systems. The application of structure-directing concepts is described using the syntheses of ZSM-18 and SSZ-26 as examples, and the control over long-range order in zeolites by structure-directing effects is illustrated by the purposeful variation of the stacking probability of SSZ-33/CIT-1 and FAU/EMT intergrowths.

Although amines have been used to successfully synthesize some high silica zeolites, they have been particularly effective in the synthesis of crystalline aluminophosphate-based molecular sieves and the concept of templating persisted. A wide variety of neutral $AlPO_4$ molecular sieve frameworks have been prepared using quaternary ammonium cations or amines, where these organic species occupy cages, channels, and intersections. Additional AlPO-based compositions and structures resulted when the framework incorporation of one or more additional elements (such as Si, Mg, Mn, Fe, Co, Zn) generated negative charge. [14] Cationic templates were still the norm, since the organic amines were predominately protonated in the more acidic synthesis media. Most of the AlPO-based molecular sieves were prepared without the need for any alkali or alkaline earth cation. In these systems the structure-directing role of the template is dominated by stereospecific space-filling and stoichiometry between the template and the framework, and is influenced to a lesser extent by framework charge compensation. With the synthesis of alkali-free forms of the CHA, ERI, FAU, SOD, and LTA structure-types, it was also clear that many structure-cation specificities are likely to be framework composition dependent.

Among the goals of zeolite science are the understanding of zeolite shape selectivity and the synthesis of new zeolite structures with desirable properties. Harris and coworkers have combined computer simulation of host/guest interactions and experimental data to understand how organic templates interact with zeolite structures. [15] In the cases of ZSM-5, ZSM-11 and SSZ-33 they found that modeling can reveal details of the complex interaction of templates with zeolite frameworks and correctly predict which silicate structure a template will make. They also observed that in the NON and CHA structure types, the zeolite template interaction energies correlate extremely well with experimental crystallization times, indicating participation of the template in the rate determining step of crystallization. [16]

A combination of several computer modeling techniques has been applied to investigate the ability of organic molecules to template microporous materials. [17] The efficacy of a template was rationalized in terms of the energetics of the host-template interactions. The calculated geometries of the template/framework combinations are in excellent agreement with the experimental structural data. The procedures used can successfully identify optimum templates for a given host. These results suggest that in the future it may be possible to design a theoretical zeolite structure and design a template to make it, all by computer simulation.

Catlow and his collaborators have recently achieved half the objective by using *de novo* design techniques (available in the computer code ZEBEDDE) to predict that 4-piperidinopiperidine would produce a previously known structure, an aluminophosphate molecular sieve with the CHA structure. The authors demonstrated the successful application of computer aided materials design, through the identification of critical parameters in the synthesis and the computational design of a suitable template, and then used the template to synthesize a microporous material possessing predefined structural and physical properties. [18,19] The material was structurally characterized using a combination of diffraction and EXAFS techniques. [20] It now only remains to design a theoretical structure and the template to make it, then use that template to make the target

structure.

Although most templating or structure-direction has been attributed to cations, the fluoride anion has also shown a templating effect in molecular sieve synthesis. [21] Fluoride has long been known to have a mineralizing (or mobilizing) effect in synthesis. This effect applies especially to silica-based materials which may thus be prepared in media with pH lower than 10-11. The structure-directing effect was found when F^- enabled the formation of three entirely novel materials (the silica form of the AST structure type, LTA-$GaPO_4$ and CLO-$GaPO_4$). In each of these structures F^- is incorporated into D4R units of the material and contributes strongly to the stabilization of the structure, as do the organic template molecules. This effect is chiefly observed when the framework has no charge or if its charges are auto-compensated. F-synthesis has been most recently exploited by Corma and coworkers to make a variety of pure SiO_2 structures. [22] In many of these structures the fluoride appears to be bonded to the SiO_2 lattice imparting a temporary negative charge to balance the cationic template charge. [23] Thermal treatment removes both F and organic.

In summary, alkali cations are most effective in templating low Si/Al zeolites from basic media. Quaternary ammonium cations are best at templating medium to high Si/Al zeolites and AlPO-based molecular sieves. Amines have been used to template AlPO-based molecular sieves and high-Si zeolites, and it is believed that the effective form of the amine is certainly the protonated form in AlPO-based synthesis and probably the protonated form even at the higher pH range typical of the high Si zeolites. Quaternary ammonium cations and amines have been very effective templates for phosphate-based structures, in general. The effectiveness, variety, availability, stability, and cost of the nitrogen-based cations as templates has not yet been rivaled.

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Verified Syntheses of Zeolitic Materials. H. Robson, editor

The pH-value and its importance for the crystallization of zeolites

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1. Introduction

The alkalinity in a synthesis batch is one of the most important parameters for the control of the crystallization of zeolites. It determines their composition and is to a great extent responsible for the type of the crystallizing product. [1-13]

Generally, the crystallization proceeds via the solution phase so that the species of silicate, aluminate, and aluminosilicate in the solution are important for the crystallization mechanism. The pH-value of the solution is determined by the total alkali content and complicated buffering equilibria of the mentioned species. [14, 15] Zeolites are usually synthesized in the presence of an amorphous gel phase. The solubility of this gel phase also depends on the alkalinity. It assures the supersaturation for nucleation and growth processes.

The composition of synthesis batches can be described by the formula:

$$MAlO_2n[M_mH_{4-m}SiO_4]\ pH_2O \qquad (1)$$

The "excess alkalinity" (m) in this formula is the difference between total alkalinity (MOH) and the alkali aluminate ($MAlO_2$) per mol of SiO_2.

$$m = (MOH - MAlO_2)/SiO_2 \qquad (2)$$

In systematic studies of the influence of the alkalinity on the product Si/Al-ratio, *m* is generally used as a critical parameter. [1-4]

A detailed discussion of the formation of zeolites has been given recently by Jansen [5] and by Feijen, et al. [6] In [7-12] thorough studies of the Si/Al ratio and the rate constant of linear growth in their dependence on *m* and *n* have been carried out for a series of zeolites.

The pH-value has been discussed in only a few papers in connection with the parameters of the crystallization. Generally, the different zeolite types crystallize within rather narrow ranges of pH. For faujasites, values between 12.3 and about 13.8 are observed. Robson has discussed procedures of a synthesis of NaY with Si/Al = 5 at pH = 11. [12] Between 11.3 and 12.7 mordenite usually crystallizes; at lower values ZSM-5 is obtained. [1,12] Donahoe and Liou have found a linear dependence of the Si/Al ratio of phillipsite and merlinoite in the pH range 13.3-13.7 in crystallization experiments from clear solutions of systems with an extremely high silica content. [13] In a series of papers, single values of the pH or pH changes before and after crystallization are reported. These differences are usually 1-2 units on the pH-scale.

Much work has been done in the analysis of the species in silicate and silico-aluminate solutions. Important results have been obtained from NMR. [14-16] A summary of this and other work can be found in the book of Engelhardt and Michel [16]. A thermodynamic analysis of these species has been undertaken by Guth, et al. [17, 18]

Generally, it was found that in the pH range of the crystallization of zeolites, the silicate is most probably present as $[SiO_2(OH)_2]^{2-}$ or $[SiO(OH)_3]^-$. Only comparatively low concentrations of higher condensed species are present at pH values above about 12.0. At lower pH the concentration of dimers and four-membered ring species increases. This range can be roughly identified with the crystallization region of the more siliceous zeolites with five-membered rings in their structure.

The aluminate is generally present in very low concentrations and is often described to be present as $[Al(OH)_3OSi(OH)_3]^-$. [16,18] A general survey of the pH-dependency of the hydrolysis

equilibria of cations has been given by Livage. [19] These data are important for syntheses with other anions present beside aluminate and silicate or aluminate and phosphate. [20]

For a more detailed investigation of the pH in zeolite synthesis, we have done thorough experiments on the connection of the pH with *m* and *n* and the Si/Al ratio of faujasites within a broad range of compositions.

2. Remarks on the Measurement of pH

Direct control of the pH during the crystallization would be desirable especially for industrial processes. However, this is difficult because zeolites crystallize at rather high pH-values. For a measurement of these values the Pt|H_2-electrode or the glass-electrode can be used.

With the Pt|H_2-electrode, in principle, very exact results can be obtained as has been shown by Lagerström [21] and Ingri [22] in very careful studies of the pH-dependency of the hydrolysis equilibria in silicate solutions. However, the Pt|H_2-electrode is not applicable for routine measurements for automatic control of a crystallizing batch in an industrial reactor.

For measurements with the glass electrode, it must be taken into account that this electrode responds to the concentration of the alkali ions as well as the H_3O^+ present in the solution. This so-called "alkaline error" becomes important at pH > 11.0, depending on the sensitivity of the electrode material. Data for different electrode materials are demonstrated in [23]. The alkaline error increases with temperature. It is advisable to follow the suggestions of the manufacturer of the electrode carefully. At high pH the properties of the glass membrane of the electrode may change with time. An obvious alternative is to take samples from the crystallizing batch and to carry out the measurement of the pH at ambient temperature. This procedure is thoroughly described in the literature.

3. Preparation of the Reaction Mixtures and pH-Measurements

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Generally, the batches for zeolite crystallization were prepared by mixing a silicate source and aluminate source and adjusting the excess alkalinity *m* with a suitable quantity of alkali hydroxide. For the present study the following sources were used:

Alumina source: 2.5 mole $Al(OH)_3$ (Merck, reinst) and 5 mole NaOH (Merck, reinst) in 1000 g solution.

Silica source: Water glass [Merck, sp. gr. = 1.37) or Silicic acid (Fällungskiesel säure, Merck) and NaOH to give 273.5 g SiO_2 in 1000 g solution.

The solutions were mixed at ambient temperature adding the silicate to the aluminate and the additional NaOH. Most of the experiments (p = 400) were carried out with a concentration of 50 g (AlO_2^- + n SiO_2) / 1000 g H_2O.

Regarding the general batch composition, $MAlO_2n(M_mH_{4-m}SiO_4)pH_2O$, the concentrations were adjusted to values of n = 2.0 - 14.0, m = 0.3 - 2.5 and p = 400. Some of the batches had lower water contents of p = 195 and p = 260.

After 2 hours homogenization an appropriate amount of nucleation gel was added to assure the crystallization of Y-zeolite, again stirred for half an hour and then the pH measured. The nucleation gel had a composition of $NaAlO_2$ 7.5 ($Na_{2.0}H_{2.0}SiO_4$) : 155 H_2O. [11] The batch was then heated to the crystallization temperature of 88°C.

After crystallization the samples were recovered and characterized as described in [7-11]. The Si/Al-ratios of the products were determined by the EDAX method in a Phillips SEM 515 and the EXAX-Analyzer PV 9900. The reaction mixtures had pH values between 12.4 and 14.1. From all mixtures faujasite crystallized. The pH measurements were done with WTW512 and a pH electrode belonging to this apparatus.

Reproducible results could be obtained according to the following procedure:

- Calibrate at pH = 7.0 using a commercial buffer solution (Riedel de Häen).
- Calibrate at pH = 13.0 using a commercial buffer solution (Riedel de Häen) and adjust the slope of

the instrument.
- Read the pH of the sample. Usually a time of about 5 minutes was sufficient to obtain a constant reading.

Between the different steps the electrode was cleaned with distilled water.

4. Discussion

In Fig. 1 the correlation of *m* and the measured pH values is demonstrated for the different Si/Al rations *n* in the batch. The relation of both quantities can be fitted by a logarithmic relation which is equivalent to a titration curve of a weak acid with a strong base at the alkaline end. For $n < 5$, the curves for the different *n* are fairly close together. For higher *n*, deviations are observed which are not demonstrated in Fig. 1. These *n* are often applied for crystallization of NaY

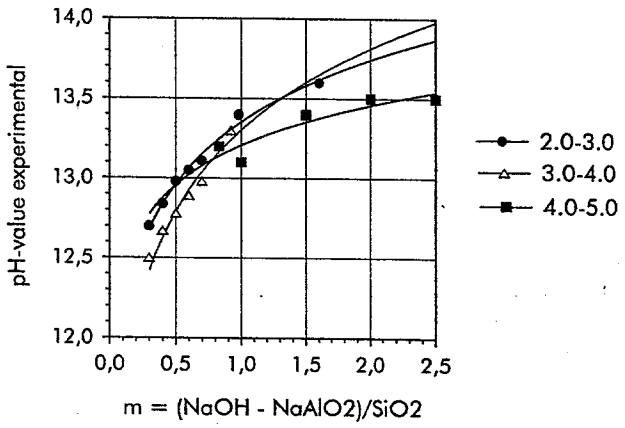

Figure 1: pH-value in the solution phase of batches with different Si/Al-rations n in dependency of the excess alkalinity m. The data have been fitted to the function pH = a + b log (cm)

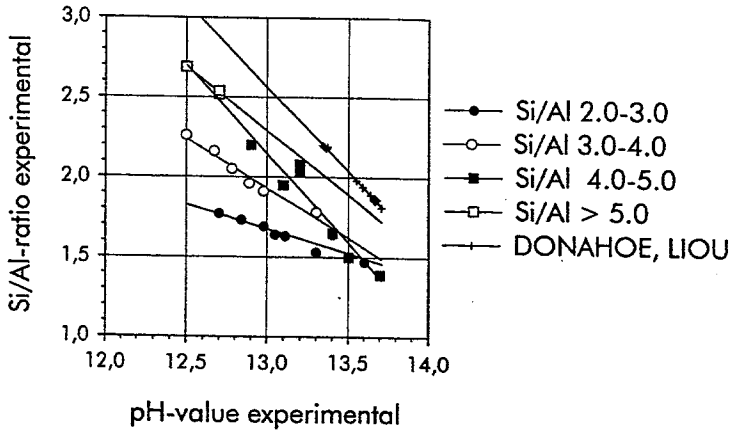

Figure 2: The Si/Al-ratio of the products in dependency of the pH - value in the solution phase for different Si/Al - ratios n in the batch

with high Si/Al ratios and also for crystallization of the more siliceous zeolites as, e.g., mordenite or ZSM-5. *m* is a more sensitive measure for the alkalinity than the pH value, apart from the advantage that it is given directly by the batch composition.

Fig. 2 shows the dependency of the Si/Al ratio of the products on the measured pH for different *n* in the batches. The crosses demonstrate results of crystallization experiment leading to phillipsite and merlinoite carried out by Donahue and Liou. [12]

The product Si/Al ratio decreases almost linearly with the pH if *n* is held constant. For increasing *n* the slope of these straight lines increases. The values for *n* = 6.0, 7.5 and 8.0 lie near the curve for *n* = 5.0. Formally, the curves for different *n* meet at Si/Al = 1.5 and about pH = 13.5.

Extrapolating the curve of *n* = 5 and 6.0, 7.5 and 8.0 in Fig. 2 to pH = 11.0 as it was suggested for the faujasite synthesis, a Si/Al ratio of about 4.0 can be obtained. [12]

Summarizing, Fig. 2 shows that for fixed *n* the Si/Al ratio of faujasites is a unique function of the pH value in the solution phase. However, for a prediction of the Si/Al ratio, the pH is not very suitable because exact pH values in the batches can be expected only after a time-consuming aging procedure.

Therefore, we have tried to find a direct relation between the parameters *n* and *m* of the batch composition and the final Si/Al ratio. [11] From extensive experiments, including studies of the concentrations of OH^- ions and the silicate in the solution phase [7-10], a simple relation could be derived which holds with great accuracy

$$Si/Al = 1 + b\frac{|SiO_2|_{sol}}{|OH^-|_{sol}} \qquad (3)$$

using $b = 2$. Eq. 3 can be explained by a simple model of the formation of zeolites. [24]

Like the pH values, the concentrations are not very suitable for practical use in the prediction of the Si/Al ratios from the initial composition of the gel. With some obvious assumptions, Eq. 3 has been changed to an empirical relation containing only *n* and *m* as parameter with the constant $b = 2$.

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$$Si/Al = \frac{(b + m)n}{(b + mn)} \qquad (4)$$

In Fig. 3 a large number Si/Al product ratios from batches for different *m* with $1.4 < n < 14.0$ are compared with values which have been calculated using Eq. 4.

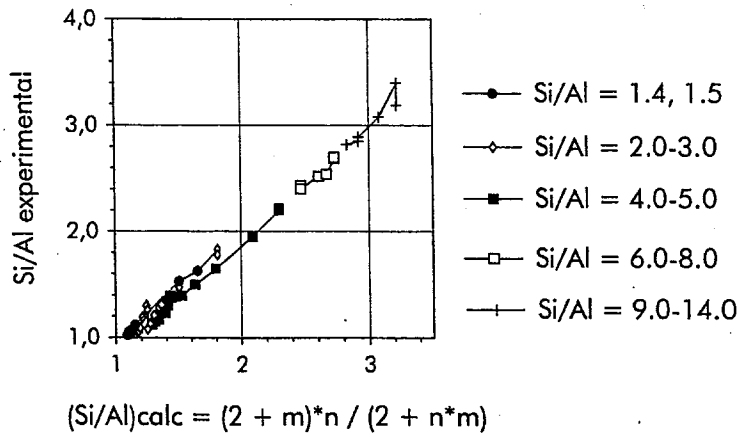

Figure 3. Si/Al - ratio of the product in dependency of (2 + m)n/(2 + nm)

It can be seen that the Si/Al ratio of the crystallizing product can be predicted by Eq. 4 over the whole range of n much more reliably than from the pH values of the solution phase.

From extensive studies of literature data, especially from [1-4] and the first edition of 'Verified Syntheses," it could be seen that Eq. 4 can be used successfully for all zeolites with four- and six-membered rings in their structure. [24] As examples, ZSM-3, LTL, Rho and offretite shall be mentioned. Data for high silica zeolites like mordenite, ZSM-5 and Beta can be described by Eq. 4 using larger values of b . [25]

Systematic arguments for a choice of b for a special zeolite are, however, missing until now. Therefore, Eq. 4 must be regarded as an empirical relationship at the present stage of discussion.

The general role of the OH^- ion as a mineralizer can be partially replaced by fluoride leading to a variety of new syntheses at lower pH values. These syntheses are usually called "low alkaline syntheses" or "fluoride route." Most probably the F^- increases the solubility of the aluminate as could be shown, for example, in kinetic experiments of the crystallization of Y zeolites. [26]

5. Conclusions

The composition and the ranges of stability of the zeolitic products depend on the pH value, the alkalinity and the Si/Al ratio present in the batch. For practical use in the planning of syntheses, the pH value is rather complicated to handle. The empirical Eq. 4 proved to be suitable for a prediction of the product Si/Al ratio from the batch composition with the restrictions discussed for high silica zeolites. Eq. 4 includes the influence of the alkalinity m as well as the Si/Al ration n of the batch.

Predictions of the kind of the crystallizing zeolite and also of the effect of templates have not been possible thus far and remain a matter of experience.

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Microwave technology in zeolite synthesis

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Microwaves have a wavelength between 1 millimeter and 1 meter which corresponds to frequencies of 300 GHz and 300 MHz. These frequencies are indicated in the electromagnetic wave spectrum in Fig. 1.

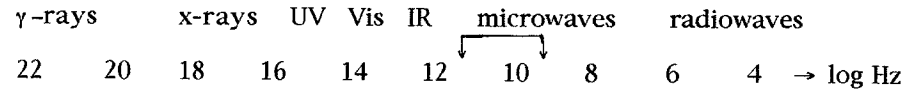

Fig. 1. Electromagnetic spectrum including microwave frequencies between infrared and radio frequencies.

As radar and telecommunication also use the microwave frequency band, only 4 specific frequencies are available for microwave heating. One of them, actually 2.45 GHz, is applied in household microwave ovens.

A microwave has an electric and a magnetic component which are in phase and perpendicular to each other in amplitude. Both wave components are perpendicular to the direction of travel. The heating effect in all types of materials that can interact with microwaves is mainly caused by the electric component. The total polarization (α_t) of the material based on the displacement of electrons, nuclei, permanent dipoles and quadrupoles and charges at interfaces is the sum of the following parameters:

$\alpha_t = \alpha_e + \alpha_a + \alpha_d + \alpha_i$: in which

α_e is the electronic polarization, displacement of electrons

α_a the atomic polarization, polarization of nuclei

α_d the dipolar polarization, polarization of permanent dipoles and quadrupoles

α_i is the interfacial polarization, polarization of charges at the interface

As both the electronic and atomic polarization operate at time scales that are smaller than required for microwave frequency field oscillations, these polarizations do not result in conversion of microwave into heat energy. The time-scale of the orientation of permanent dipoles is, however, comparable to the time scale of microwave oscillations. Thus when the amplitude of the electric field increases, the dipoles align themselves accordingly. Next, as the field amplitude decreases to zero intensity, the dipoles return to their random orientation. The change in orientation in both operations results in an energy conversion from electric into thermal energy. The interfacial polarization contributes to dielectric heating when conducting particles are suspended in a non-conducting phase. This effect is not substantial at microwave frequencies and thus results in a modest contribution to the heating. Conduction effects can also contribute to the dielectric heating. Since ions are charged, they accelerate in an electric field. Herein, the electromagnetic energy is converted in kinetic energy which is transferred to neighboring molecules resulting in unordered kinetic energy, actually heat.

The way the above mentioned materials react on microwaves is determined by their dielectric constants. The complex dielectric constant ε can be expressed as:

$\varepsilon = \varepsilon' - i\varepsilon''$; in which:

ε' is the real component

ε'' is the imaginary component and

i is $\sqrt{-1}$, indicating a 90° phase shift between ε' and ε''

The real part, or relative permittivity, represents the degree to which an electric field may build up inside a material when exposed to an electric field. The imaginary part, or dielectric loss, is a measure of how much of that field will be converted into heat. The loss angle δ is the phase difference between the electric field and the polarization of the material. The loss angle as formulated below is referred to as the dissipation factor.

$$\tan \delta = \varepsilon'' / \varepsilon'$$

The dissipation factor, or tan δ is a measure for the material's ability to transform electromagnetic energy into heat. The higher the dissipation factor, the better the transformation of microwave energy into heat. In Table 1, dissipation factors are given for relevant materials.

It is clear from Table 1 that water, and particularly water with a high Z-value, has a high ability to transform microwave energy into heat. Materials that are not heated by microwaves are, for example, glass and Teflon.

The dielectric constants of the materials also determine the penetration depth, which is defined as the depth into the material where the power is reduced to about 1/3rd of the original intensity.

The penetration depth is formulated as:

$D_p \propto \lambda \sqrt{(\varepsilon'/\varepsilon'')}$, in which:

λ_o is the wavelength. Thus a material with a higher dissipation factor will have a lower penetration depth. The wavelength and hence the frequency also greatly influences the penetration depth. From the above it is clear that the sample size, the penetration depth and heating rate are coupled and can result in a homogeneous or heterogeneous heating of the material.

Thus in case a fast homogeneous heating is preferred, the material, for example a zeolite synthesis mixture, must have a relatively high dissipation factor, a high external surface and small volume. In the case of water this phase must have the form of a thin disk. At the same time one should take into account the microwave frequency applied. Higher frequencies will give smaller penetration depths. In case of extremely fast heating of zeolite syntheses mixtures, boiling point retardation might occur which results in small, but uncontrollable, explosions.

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Table 1. Dissipation factors of relevant materials for zeolite synthesis

Material	tan δ x 10^4	microwave frequency (GHz) 2.45	3.00
Teflon	2.1 x 10^{-4}	+	
Glass	4.0 x 10^{-4}	+	
Benzene	14 x 10^{-4}	+	
Ice	9.0 x 10^{-4}	+	
Water	0.157		+
0.1 M NaCl	0.240		+
0.5 M NaCl	0.625		+
methanol	0.640		+
ethanol	0.250		+
ethylene glycol	1.000		+

In general it is concluded that microwave effects, particularly for zeolite syntheses, are mainly recognized as converting microwave energy into heat. There are still many contributions in literature stating that microwaves do influence the reaction rate and product distribution on a molecular scale. However, microwave photons that have intrinsically a power not much larger than ~ 10^{-5} eV at 2.45 GHz are too small and not applicable for molecular activation as compared to those encountered , for example, in UV photochemistry.

In zeolite syntheses heated with microwaves [1], the inexpensive set-up (~$1,500), compared to commercially available ovens including autoclave equipment (~$30,000), comprises of [2]:

* An ordinary household microwave oven, one of the larger types to avoid local hot spots, with a controllable temperature setting in steps of 100 W up to 1000 W.
* An autoclave, with walls of 1 cm in thickness, of Teflon, very low dissipation factor and thus transparent for microwaves (see Table 1), which is supplied with 1) a rupture disk that is connected to a hose to exhaust in case of malfunction, like boiling point retardation, the synthesis mixture and 2) a small hole through which the sleeve of the thermocouple goes into the synthesis solution/mixture.
* A thermocouple in a sleeve and a recorder. The metal sleeve must be connected to earth and resistant to zeolite syntheses mixtures.
* Perforated metal shields in the form of cylinders that can be placed around the Teflon autoclave. This way microwave radiation at a setting of 100 W can be reduced to 20, 40, 60 or 80 W. Reduced and homogeneous radiation is needed to keep the temperature in the synthesis mixture constant after an initial heating up with hundreds of watts.

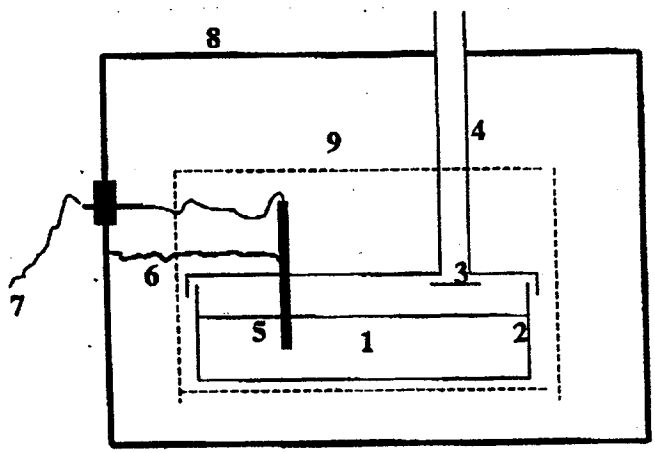

Figure 2. A general picture of the set-up in a household microwave oven to perform zeolite syntheses. [1,2]

1) zeolite synthesis mixture
2) 1 cm thick Teflon autoclave (up to 170°C)
3) rupture disk
4) exhaust channel
5) metal sleeve around thermocouple
6) connection of sleeve to earth
7) connection thermocouple to recorder
8) microwave oven
9) perforated metal shield around the autoclave.

The synthesis is carried out as follows: A regular, not viscous synthesis mixture of a zeolite is placed in the Teflon autoclave. The autoclave is closed and the thermocouple connected. An initial heating step is then applied which can be up to 1000 W. In this way the mixture is at the

projected synthesis temperature within tens of seconds. Subsequently the synthesis mixture must be kept at a constant temperature. The minimum oven setting is 100 W which is too high to compensate for the heat losses. Thus a lower power which is needed is accomplished by reducing the amount of radiation at 100 W. This is achieved with a screen of perforated metal installed around the autoclave. At a setting of 100 W and depending on the size of the holes in the perforation, only a few tens of watts will reach the autoclave and thus maintain the synthesis temperature at the projected value.

Crystallization times of zeolites were reduced to two minutes in particular cases. The main advantage of microwave heating compared to conventional heating is the high, even extremely high, up to 170°C in 20 seconds, controllable heating rates under homogeneous conditions, if the right configurational dimensions are applied.

One aspect, the formation of *pure* product, is of interest if microwaves are applied as heating technique for zeolite synthesis mixtures. The formation of pure product is related to the heat-up rate which is different in conventional heating compared to microwave heating as given in Tab. 2.

Table 2. Autoclaves of 0.5 liters were used. Stainless steel in a preheated hot air oven and Teflon in a microwave oven.

Mode of heating	projected synthesis temperature (°C)/time (minutes)	
Conventional	100 / 30	170 / 60
Microwave	100 / 0.2	170/ 0.3

If sources, in particular silicate and aluminate, are not extremely well mixed, and immediately after the mixing step exposed to rapid heat-up with microwaves, it is most likely that a mixed product distribution is observed. The product contains partly zeolite, silicate, aluminate and mixtures thereof, not yet converted into zeolite. [1] This is not observed a) after extensive stirring of the mixture at room temperature and subsequently immediate exposure to microwaves or b) after relatively short stirring and next placed in a preheated hot air oven. Apparently the nutrients need to be mixed on a molecular scale to obtain pure zeolite. This is achieved either through extremely long stirring after which the pure zeolite phase forms immediately when the projected synthesis temperature is rapidly reached with microwaves, or slowly heating up the synthesis mixture in a hot air oven which allows for further mixing upon heating up for a relatively long time before the projected synthesis temperature is reached.

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Preparation of zeolite membranes

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1. Introduction

Separation processes are widely used in industry since the chemical conversions are often incomplete. Membrane technique is one of the most attractive separation methods because of its low cost and high selectivity. A membrane is an intervening phase acting as an active or passive barrier between phases adjacent to it under a driving force. Zeolitic membranes have gained considerable attention during the last decade. Detailed information can be found in the current literature and in several excellent reviews dealing with the subject of zeolitic membranes which have appeared over the last five years. [1-7]

The regularly structured pores and cages make the zeolites a unique material for designing thin films, coatings and membranes that can be utilized for a variety of purposes. Since the early 1990s, intensive research efforts have been underway to develop the synthesis and separation applications of zeolitic membranes. The specific properties of zeolite membranes which have attracted the attention of academic and applications scientists are: (i) long-term stability at high temperature, (ii) resistance to harsh environments, (iii) resistance of high pressure drops, (iv) inertness to microbiological degradations, and (v) easy cleanability and catalytic activation.

One of the most challenging problems in the preparation of zeolitic membranes is the complete exclusion of pinholes from the membranes, particularly under conditions of severe thermal cycling.

2. Preparation of zeolitic membranes

Zeolitic films and membranes are completely different from simple crystalline zeolite powders and their preparation requires new strategies. Methods which have been developed for the preparation of zeolite membranes are as follows:

2.1. Zeolite-filled polymeric membranes

One of the most direct methods of preparation of zeolite-containing membranes is to embed zeolite crystals in a matrix. [2,6] Sealing the gaps between zeolite crystals with a gas-tight matrix can provide a membrane configuration. The application of this method of membrane preparation, however, is limited. The clogging of zeolite pores by the matrix is a serious concern. Furthermore, gaps between binder and zeolite or a porosity in the matrix could introduce nonselective diffusion pathways.

2.2. Free-standing zeolite films

For molecular sieving applications a dense, pin-hole free zeolite film with limited thickness (<1 μm) would be an ideal configuration. Such films have been grown on temporary supports like Teflon and cellulose or at the interface between two phases. [2,6] This route for the preparation of zeolitic membranes is abandoned now because of the fragility of self-supported zeolite membranes.

2.3. Supported zeolite membranes

The most frequently used and probably the most promising seems to be the so-called composite membranes. This type of membrane is prepared by *in situ* hydrothermal synthesis. A relatively thin zeolite layer is crystallized on the surface or in the pores of a pre-shaped porous support. Among different types of inorganic materials, like ceramics, metal glasses, carbon used as

supports, porous alumina has been the most popular for these preparations. The nucleation and crystal growth on the support can be self-induced or induced by attachment of seed crystals on the substrate. The latter procedure requires a pretreatment of the support before the hydrothermal synthesis. [7]

Zeolite-containing composite membranes have been prepared by a vapor phase transport method called "dry synthesis." The zeolite layer in this case is prepared by conversion of a previously deposited silica or silica-alumina layer under joint action of vapors containing water and a structure-directing agent. [4]

The zeolite type prepared most often as a membrane is MFI, which is interesting for industrial applications with its suitable pore diameter, high thermal and chemical stability, easy synthesis and modification of the chemical composition. The experience gained in the preparation of MFI and other zeolitic membranes has shown that as well as the pin-holes there are many factors critical for the performance of the composite membranes. Some of them are (i) the adhesion of the zeolite layer on the support surface, (ii) the difference of the thermal expansion coefficients of support and zeolite, (iii) the orientation of zeolite crystals, (iv) the thickness of the zeolite layer, (v) the anisotropy of mass transport due to an anisotropic pore geometry, and (vi) the influence of crystal boundaries on the permeation properties.

3. Concluding remarks

The first zeolitic membranes are already on the market. Nevertheless, the control and fine tuning of the properties of the zeolite-containing membrane configurations remains a challenge. A common problem is that, despite the use of a pre-defined methodology, it is difficult to obtain membranes with consistent and predictable properties. However, the steeply increasing interest in this field suggests that zeolitic membranes with excellent separation properties will soon be available.

Lately the zeolitic membranes have attracted considerable attention for catalytic membrane reactors, where the zeolite phase can carry the dual function of separator and catalyst.

Other potential applications of zeolite film and layers include chemical sensors, zeolite electrodes, solar energy conversion, zeolite batteries, optical and data storage materials.

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Verified Syntheses of Zeolitic Materials. H. Robson, editor

Safety considerations for zeolite synthesis

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In general, synthesis experiments are neither complex nor hazardous, and normal precautions which apply to any chemistry laboratory are adequate to protect both equipment and the investigator. But certain precautions should be called to the attention of the inexperienced operator.

1. Source Materials

Silica and alumina are inert in most forms, but ingestion of dust should be avoided. The alkoxides are skin irritants and should be handled with gloves and in a hood. Hydrofluoric acid (HF) is corrosive and skin contact or inhalation must be avoided. Likewise strong caustic is corrosive to skin and equipment. Gloves and a face mask are indicated, and the experiment should be done in a hood.

In one case an "overflow" occurred when an inexperienced student put all the powdered aluminum required for a synthesis into a caustic solution. The exothermic dissolution heated the solution, accelerated the dissolution autocatalytically, and resulted in "boil over." Obviously, if hydrogen is given off, danger of explosion exists. The use of aluminum wire, which dissolves more slowly, is suggested.

Organic templates cover a wide range of volatility and toxicity. In many cases these materials are quite rare and their toxicity may not be well defined. Some are known to be biologically active; in all cases the investigator should avoid skin contact or inhalation by using gloves and working in a hood.

In some cases, the potential exists for explosive decomposition of the template under crystallization condition. There is no good way to rule out this possibility, but a strong exotherm in the thermal analysis curve of the template indicates it should be treated with caution.

No preparations in this book use beryllium (Be) or thallium (Tl), but reports can be found in the literature of zeolite syntheses using these materials. Be and Tl are extremely toxic and should be used only by experts who thoroughly understand the necessary precautions.

2. Batch Preparation

The hazards of handling strongly caustic materials are increased when the solutions are hot. Gloves and face mask are still more important. Hydrolysis of the alkoxides produces heat; this may not be a problem in gram quantities but becomes so with scale-up. The alcohol produced is often removed by evaporation which can be a fire hazard. High-speed mixers can be splash hazards unless totally contained.

3. Crystallization

Zeolite crystallization is usually done at autogenous pressure at temperatures up to 200°C. With water present, this can mean pressure up to 15 atm. When organic templates are present, the pressure can be considerably higher. The manufacturer's specifications for the autoclave must be carefully considered. The liquid fill of the cold autoclave should not exceed 75%; the expansion of liquid water between 25 and 200°C is not negligible. Teflon loses its strength above 200°C. Teflon gaskets and liners must be treated with caution at these temperatures. When working in metal autoclaves without liners, stainless steel exposed to caustic mixtures undergoes caustic embrittlement at temperatures above 200°C, which can quickly ruin an autoclave. To clean autoclave liners between experiments, strong, hot mineral acids are usually used, for example HNO_3. It takes copious amounts of rinse water to remove all the acid.

Polypropylene jars may be used for crystallizations below 100°C. After extended use, they

tend to spring a leak, as the bottom begins to separate. Although there is no danger of the jars bursting at this temperature, organic vapors are liberated, so that the oven or bath used for heating should be placed under a hood or have otherwise good ventilation.

Sealed quartz tubes are often used as the crystallization container, especially for small quantities and high throughput. Also one can monitor progress of crystallization visually. Quartz is a poor conductor of heat, but prolonged heating for sealing can heat the synthesis batch to boiling if the neck is too short. After crystallization, the quartz reactor should be opened behind a shield to protect the operator in case of residual gas pressure.

Heat transfer by air, for example in an oven, is slow, and heating in a bath is preferred. As heating fluid, a polyglycol-type, which does not attack polypropylene, is recommended. A silicon oil leaches plasticizer out of the polypropylene thus making the jar brittle and subject to cracking. Glycerol can be used, but has a relatively high vapor pressure (vapors condense on all surfaces in the lab making them sticky) and should be used under a hood. The temperature controls of a liquid bath should have a high-temperature shut-off to prevent overheating, in case the temperature controller fails.

Combinations of organic templates and strong oxidizing agents such as chromate and permanganate are potential explosives, particularly in low-water conditions.

4. Product Recovery

Opening the reaction vessel after crystallization should be treated with caution. Even thoroughly cooled, residual gas pressure should be expected. Organic templates may degrade during the reaction; the products may be toxic and often cause a stench problem. The mother liquor after a templated synthesis may be a disposal problem. In most cases it should be collected for disposal as a hazardous chemical.

The synthesis batch may crust over during crystallization and retain residual gas pressure. When the crust is penetrated, the contents may constitute a splash / missile hazard.

A template not removed by washing us usually expelled by calcination. The template or its decomposition products are usually combustible and it is easy to start a fire. The heating equipment should be properly vented; if necessary nitrogen blanketed.

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**With contributions by Kenneth Balkus, Günter Kühl and Robert Thompson*

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Verified Syntheses of Zeolitic Materials. H. Robson, editor

Product characterization by x-ray powder diffraction

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1. Introduction

Different features of a powder diffraction pattern can be exploited in the characterization of a material (see Table 1). Of course, powder diffraction data is most commonly used as a "fingerprint" in the identification of a material, but the other information that can be gleaned from a diffraction pattern should not be forgotten. If possible, the diffraction experiment should be adapted to optimize that feature which provides the information desired.

Table 1. Information contained in a powder diffraction pattern

Feature	Information
Peak positions (2ϑ values)	Unit cell dimensions
Non-indexable lines	Presence of a crystalline impurity (or incorrect indexing)
Systematically absent reflections	Symmetry
Background	Presence (or absence) of amorphous material
Width of peaks	Crystallite (domain) size
	Stress / strain
	Stacking faults
Peak intensities	Crystal structure

Although there are a number of different powder diffractometer geometries on the market, each one with its positive and negative attributes, all have an X-ray source, a specimen holder and a detector, and almost all are capable of recording a respectable powder diffraction pattern. The difficulty arises when one wants to compare data from different instruments or even from the same instrument with different operators. It is not possible to go into detail in the space available here, but the basic considerations and a few common sources of error will be discussed. For more information, the reader is referred to the volume entitled "Modern Powder Diffraction" edited by Bish and Post [1] or to the article entitled "Practical Aspects of Powder Diffraction Data Analysis" by Baerlocher and McCusker [2].

2. Data Collection

2.1 Peak positions

If the pattern is to be indexed (Miller indices *hkl* assigned to each of the peaks and thereby the unit cell dimensions extracted from the pattern), it is essential that the peak positions be determined accurately. In this case, the instrument's 2ϑ scale needs to be carefully calibrated using a standard material such as the NIST silicon standard 640b. The sharper a peak, the better its 2ϑ value can be determined, so the diffractometer should also be adjusted to optimize resolution. As a guide, almost any laboratory instrument can be adjusted to give a full width at half maximum (FWHM) for the Si 111 reflection (28.44°2J with CuKa1 radiation) of 0.10°2ϑ or less. The measured 2ϑ values for the peaks in the standard material's pattern should agree with the literature values to within 0.01°2J.

If the sample is off-center, this will affect the 2ϑ zeropoint correction, so ideally, the sample should be mixed with a small amount of the standard (that is, measured with an internal standard), so that the 2ϑ calibration can be done simultaneously. However, if care is taken in positioning of the sample, a 2ϑ calibration using an external standard is usually sufficient. In reflection mode,

thin samples are preferred for peak position determination, so effects of sample transparency can be eliminated.

2.2 *Peak intensities*

For indexing purposes, the intensities of the peaks are irrelevant, but for identification or for structure analysis, accurate relative intensities are essential. There are three commonly ignored factors which can severely affect the relative peak intensities: 1) sample thickness, 2) preferred orientation, and 3) divergence slit(s).

Bragg-Brentano reflection geometries require an "infinitely thick" sample. That is, it is assumed that the sample is thick enough that all the X-rays interact with the sample (by absorption or diffraction) before they reach the sample holder. In this way, the volume of sample effectively irradiated remains constant as 2θ changes. If this is not the case, the intensities must be adjusted for the transparency of the sample. In general, the relative intensities of the low angle reflections will be too large if the "infinite thickness" criterion is not met. For transmission geometries, on the other hand, the sample must be thin enough that the X-rays are not too strongly attenuated.

Most powder diffraction data analyses assume that the sample consists of millions of randomly oriented crystallites. If this is not the case, relative intensities will be distorted. For example, if the crystallites have a plate-like morphology, they are likely to lie flat. Assuming that the *c*-axis is parallel to the short dimension, crystallites aligned in the *001* diffraction condition will be overrepresented, and those in the *hk0* diffracting condition underrepresented. This will then lead to a bias in the relative intensities recorded. Various sample preparation techniques have been used to reduce preferred orientation (such as back or side loading of flatplate sample holders, mixing amorphous glass beads with the sample, or spray drying), but none is foolproof. Measurements in transmission mode with the sample loosely packed in a rotating capillary are less susceptible (but not immune) to this problem. An easy way to establish whether or not preferred orientation is present is to measure the diffraction pattern in both reflection and transmission mode. The two measured patterns should be comparable, and if their relative intensities differ significantly (in an *hkl*-dependent manner), there is probably preferred orientation present in the sample.

At low angles, the X-ray beam is spread over a larger surface of the specimen than it is at high angles. To ensure that the X-rays interact only with the sample (and not the edges of the specimen holder) a slit is inserted between the X-ray source and the sample to confine the beam to the sample (divergence slit). As the 2θ angle increases, this slit can be opened wider to allow more X-rays through and thereby increase the counting rate, but then the resulting data must be corrected for the increased volume of sample irradiated. The slit size can be varied during the measurement either continuously (using an automatic divergence slit) or manually (using a series of calibrated slits). For data comparison purposes, the data should then be transformed to constant sample volume (single constant slit) data. In many laboratories, data are recorded using a relatively wide single slit that is appropriate for higher angle data, but not for the lower 2θ values. In such a measurement, the relative intensities of the low angle peaks will appear to be too low, because only a part of the X-ray beam interacts with the sample.

3. Identification

In a zeolite laboratory, powder diffraction data are most commonly used to identify a newly synthesized material or to monitor the effects of a post-synthesis treatment. In both cases, the measured pattern is compared with an existing one, whether it be a pattern in the *Collection of Simulated XRD Powder Patterns for Zeolites* [3], the Powder Diffraction File (PDF) of the ICDD [4] or an inhouse data file. Such comparisons are not easy for zeolites, especially if the data collection or sample preparation conditions differ. A few practical considerations are presented briefly below.

(1) Intensities are important for identification, so the data should be collected bearing the points discussed in the previous section in mind.

(2) Data should be in the form of a constant volume measurement if the *Collection*, the PDF or any of the common databases is to be used in a search/match process.

(3) Peak position information is often given in terms of d-values rather than 2ϑ values, because d-values are independent of the X-ray wavelength (λ) used. ($d=\lambda / 2 \sin\vartheta$)

(4) The low angle lines are the ones most strongly affected by non-framework species (see Ref. [2] p. 418). In general, these lines are more intense in the calcined material than in the as synthesized form, and similar materials containing different cations or different organic species may have quite different relative intensities at low angles. However, the intensities of the higher angle reflections are generally dominated by the positions of the framework atoms, so these can be compared quite well.

(5) Different synthesis conditions or different post-syntheses treatments can cause subtle distortions in a zeolite framework structure that can complicate identification. The symmetry may be reduced (and thereby produce many more peaks in the pattern), although the basic framework topology (connectivity) remains unchanged. In such a case, indexing the pattern to obtain the dimensions of the unit cell can facilitate the identification.

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Verified Syntheses of Zeolitic Materials. H. Robson, editor

Determination of the elemental compositor of zeolitic materials

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1. Introduction

The determination of the bulk elemental composition of zeolites is of importance in many aspects of zeolite synthesis, characterization and applications. This information is used to verify the synthesis formulations, the bulk silica/alumina ratio, the cation(s) concentration, degree of ion exchange, and the detection of contaminant elements (impurities, poisons). The elements of interest can be grouped into two broad categories, metals and non-metals. The latter commonly include sulfur, chlorine, carbon and nitrogen. Generally the results are reported on volatile free basis, thus the Loss on Ignition (LOI) at a specified temperature and time is also determined. The concentration of water is determined if the request is for the results to be based on anhydrous basis and volatile components other than water are present. The information herein is a brief review of the techniques and their characteristics as used for the determination of bulk elemental compositions of zeolites.

2. Determination of metals

The most common techniques for the determination of compositional metals are Inductively Coupled Plasma Emission Spectroscopy (ICP), Atomic Absorption Spectroscopy (AAS) and X-Ray Fluorescence Spectroscopy (XRF). Because these methods offer the benefit of reduced interferences and matrix effects, and have improved accuracy, precision and speed, the use of "classical wet chemistry" methods (for example, gravimetric silica, titrimetric or spectrophotometric alumina) has been greatly diminished.

ICP is probably the most widely used technique for the determination of the elemental composition of zeolites. It offers the capability for the simultaneous (or sequential) determination, with good sensitivity and precision, of most compositional matrix metals of interest, for example silicon, aluminum, phosphorous, titanium, and many others. Relative standard deviations of 1% can be routinely obtained for the major and minor compositional metals. In general, the sensitivity of ICP is better than that possible with conventional flame AAS for most refractory-like metals and phosphorus. However, flame AAS has somewhat better sensitivity for Group IA elements, including sodium and potassium, and relatively similar sensitivity for many metals of interest, such as calcium, magnesium and iron. Because the cesium emission lines are above 800 nm, conventional ICP instrumentation is incapable of its determination and AAS has to be utilized.

Wavelength dispersive X-Ray Fluorescence (XRF) is also used for the determination of the elemental composition of zeolitic materials. As compared to ICP/AAS, the benefits of XRF include the ability to determine some non-metals, conceptually simpler sample preparation and improved precision. Relative standard deviations of ~0.1 to 0.2% are possible for samples introduced as glass discs. The disadvantages include poor sensitivity for light elements and sensitivity to changes in the matrix composition. This means that in many cases XRF can not perform the complete characterization. ICP/AAS has to be employed for some of the determinations, for example, lithium and low concentrations of sodium. Also, especially for best accuracy, changes in the matrix compositional elements require the use of matrix matched calibration standards and the use of mathematical models. Thus XRF has its greatest impact in a controlled, manufacturing environment, while in an R & D environment ICP/AAS is often the technique of choice.

3. Sample decomposition for ICP and AAS

Both conventional ICP and AAS require that the sample be introduced as a liquid, thus decomposition is necessary prior to analysis and similar preparation schemes apply for both techniques. There are two main approaches for sample dissolution in order to determine major and

minor compositional elements (including silicon). The sample can be solubilized by a fusion with lithium tetraborate (or a similar flux) followed by dissolution of the flux in dilute hydrochloric acid, or it can be digested with acid in a beaker.

a. Beaker digestion for ICP or AAS analysis

Although this approach is used widely and can produce good data, it has several areas of concern. The acid digestion may not completely solubilize binders, such as clay. Increasing the severity of the decomposition conditions (e.g., higher temperature) can generally ensure complete dissolution, but such a modified digestion may require elevated pressures in a Teflon lined bomb. The digestion requires the addition of hydrofluoric acid in order to solubilize the silicon, and because of the volatility of the resulting fluorides, special care must be taken to avoid the loss of silicon.

A more serious problem is the fact that fluoride will attack a conventional ICP sample transport system that contains quartz/glass components, thus necessitating the complexation of the fluoride. This can be accomplished utilizing boric acid, or a commercial complexing agent. In the author's experience these solutions mostly extend torch life, they do not completely eliminate attack on the quartz and thus accurate determination of silicon is not possible. Hydrofluoric acid resistant sample transport systems are available from instrument manufacturers. We have found these to be inadequate because the typical alumina sample delivery torch tube is attacked by fluoride thus contributing to increased aluminum and silicon (impurity in the alumina) backgrounds. Replacing the alumina tube with sapphire eliminates this problem, unless very high concentrations of fluoride are present. [1] A commercial sapphire torch tube is currently available from at least one manufacturer.

Typical AAS sample introduction systems are silica free and the fluoride containing solutions can be analyzed, but the precision for silicon and aluminum is generally inadequate. If the silicon is of no interest, these issues, except for completeness of dissolution, become irrelevant. In fact, for the determination of minor and trace metals, it is often desirable to volatilize the silica during sample decomposition, thus reducing the total dissolved solids.

b. Dissolution by Fusion for ICP or AAS analysis

It is the author's experience that sample dissolution by fusion results in better precision and accuracy than possible by a beaker digestion. Although other fluxes can be used, the author fuses the sample, in a platinum crucible, using a 15:1 ratio of lithium tetraborate to sample. The fusion can be accomplished using automated fusion devices, via a muffle furnace or air boosted natural gas burners. The resulting melt is allowed to cool to room temperature and is then dissolved with dilute (5-10%) hydrochloric acid. In case of the automated devices, the hot melt is poured directly into the dilute acid. This is preferable as it enables faster and less troublesome dissolution. In order to facilitate the pouring of the hot melt, a small amount of cesium iodide (same weight as the sample) is weighed into the platinum crucibles together with the flux and the sample material.

4. Sample preparation for X-ray fluorescence analysis

There are two main approaches utilized for sample preparation in order to achieve the best precision for major compositional elements. The sample is fused akin to the fusion described above. The resulting hot melt is poured into a platinum mold and forms a glass disc that is introduced to the XRF. While a number of fluxes can be used, lithium tetraborate is often the flux of choice for zeolitic materials. In order to reduce the sensitivity of XRF to the matrix composition, lanthanum oxide (20%) can be added to the lithium tetraborate flux. A number of approaches can be taken in order to prepare calibration standards; however, the fusion based sample preparation approach enables the addition of elements of interest (usually as oxides) directly into the platinum crucible prior to the fusion.

Pressing pulverized samples into pellets is also a viable approach. The drawback is that this technique is likely to have poorer precision than the fusion and be more sensitive to changes in the matrix composition. However, it is satisfactory for many applications and it enables the

determination of non-metals, such as halogens and sulfur, that would be volatilized during the fusion. Often, if the desired precision can be achieved, the samples can be introduced to the XRF simply as ground powders, without pressing The author routinely determines sulfur and chlorine with a detection limit of 100 ug/g.

5. Determination of non-metals

a. Determination of carbon, hydrogen and nitrogen (CHN)

The determination of CHN is generally requested because these elements are present in an organic amine template used during synthesis or because the zeolite adsorbs these during a specific application. In either case conventional CHN analyzers are frequently used for this determination. Alternative approaches include the determination of nitrogen by classical Kjeldahl digestions and the determination of carbon by combustion analyzers specific for only carbon. The hydrogen concentrations from a CHN will include hydrogen from water and hydrocarbons. Karl-Fischer based determination of water, at specified temperature, can be used to differentiate the two sources of hydrogen.

b. Determination of sulfur

The determination of sulfur is generally accomplished via a combustion type analyzer, often together with carbon. Commercial equipment exists for single or multi-element analysis of C, H, N, and S. There are several alternative non-oxidative techniques; these include XRF with a detection limit of about 100 ug/g, or specialized reduction-distillation of the sulfur as hydrogen sulfide followed by calorimetric detection via methylene blue.

c. Determination of chlorine

The determination of chlorine can be accomplished via a variety of leaching or closed vessel (microwave) digestions followed by silver nitrate titrations of the liberated chloride. Alternatively, leaching (which may include full dissolution by addition of hydrofluoric acid) followed by Ion Chromatography has been found very useful as it enables the detection of chloride as well as nitrate, sulfate and ammonium. Also, XRF can be used, with a detection limit of about 100 ug/g chlorine.

d. Determination of fluorine and chlorine via pyrohydrolysis [2]

A specialized technique has been implemented for the determination of fluorine. The sample is pyrolyzed in a nickel combustion tube in a steam atmosphere at 1000°C. The steam/analyte eluent is scrubbed and the fluoride concentration is then determined via Ion Chromatography or Ion Selective Electrode. Chlorine is volatilized together with the fluorine and can also be determined.

6. Summary

All the techniques described herein have their strengths and weaknesses and areas of overlap. The selection is dictated by specific sensitivity and precision requirements and by instrument availability. Each approach described above can be modified to address specific requirements. For example, a graphite furnace and hydride AAS can be used with great sensitivity for the determination of trace contaminants such as arsenic or mercury.

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Verified Syntheses of Zeolitic Materials. H. Robson, editor

Characterization of zeolites by SEM

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1. Introduction

In the scope of this contribution the reader is referred to the regular textbooks for technical information on the Scanning Electron Microscope (SEM).

The resolution of SEM in the world of microscopy clearly bridges Optical Microscopy (OM) with Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) as is depicted in Figure 1.

The size of the zeolites that can be studied with SEM is thus between 20 nm and 20 μm.

Regarding zeolite sample preparation, two approaches are possible: for the ultimate picture and for fast exploration.

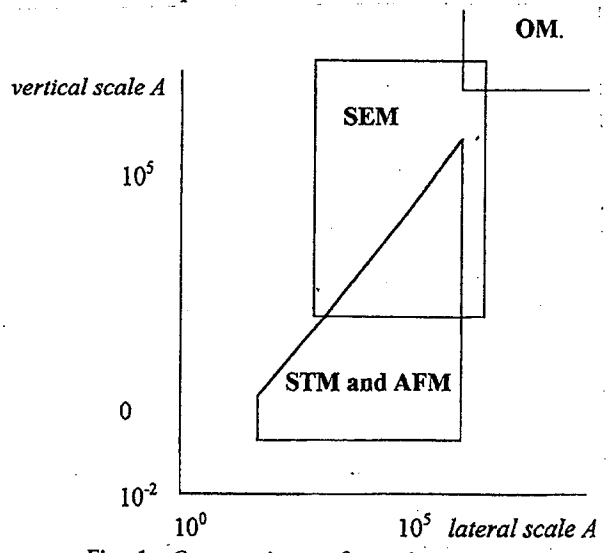

Fig. 1: Comparison of resolution between OM, SEM and STM)

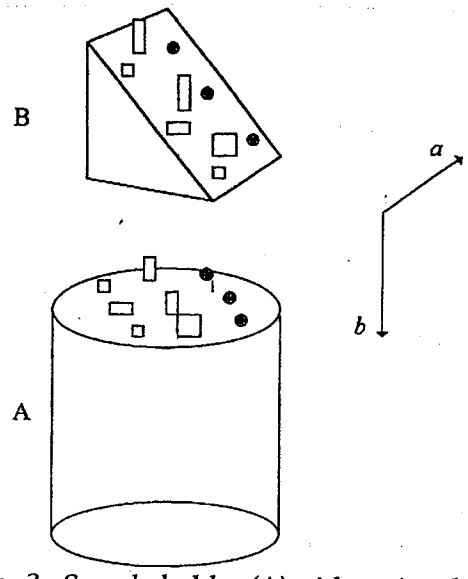

Fig. 2: Sample holder (A) with optional prismatic holder (B). Three rows of samples are shown. Rotation axis are indicated.

2. Approach for the ultimate picture

Start with a metal holder of which the surface is polished. The background is then smooth and even and does not interfere with the contours of the crystals.

Bring a hair from your head in contact with a glue in a way that you get individual small drops of glue on this hair. Touch the sample holder with this hair and a row of very tiny spots of glue are now present on the holder. Either powder or, preferably, crystal(lites) can be fixed on this row of glue spots, thus representing one type of zeolites. More rows with the same or another zeolite material can be arranged this way on one sample holder. Next, the samples need to be coated via a sputter technique with a conduction layer of preferably noble metal. This layer must be thin so that details of the sample are not blurred. Thus, in the case of an Edwards sputtering chamber, one minute for gold at the proper setting is enough.

In case the crystals are very small (< 0.1 μm) or flat oriented on the support, it is difficult to make a picture of the crystallite with enough contrast to the background, actually the support. To

observe the crystal clearly it is convenient to use an additional prismatic shaped support that is mounted on the primary support as shown in Figure 2. Not only the form, but also the aspect ratio of crystals, can be well studied. In particular, the crystal size and aspect ratio of crystals are determined with accuracy only when a crystal face is oriented perpendicular to the beam. With the additional support, the crystal can be oriented either perpendicular to the beam, which means rotation around the lateral axis as indicated in Figure 2, or almost parallel to the beam. With the rotation around the axial axis *b*, shown in Figure 2, at least three crystal faces perpendicular to each other can be studied on one crystal.

Regular sample tables of SEM apparatus only rotate thirty degrees in the lateral orientation.

3. Approaches for fast exploration

Start with a metal holder on which a preshaped, double-sided, sticky, conducting layer is applied. Divide the sticky area in, for instance, six segments. Dust each segment with a sample and remove loose material. Sputter for one or two minutes. Pictures can now be made.

In all cases the samples need to be dry and/or free of volatile material in the high vacuum chamber.

The information that can be drawn from SEM pictures of zeolites is given in Table 1.

Table 1. Subjects and details that can be observed.

Subjects	Details
Crystal form	Type of zeolite
	Aspect ratio
	Influence on crystal growth, for example, inhibition of crystal faces that indicate the presence of an unknown factor
	Crystal size distribution phenomena, for example, aggregation / twinning / intergrowth
	Indication of single crystals
External surface	Relative roughness
	Secondary nucleation effects
Purity of the phase	Other zeolite types
	Amorphous material
Unknown species	New material?

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Product characterization by NMR

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The impact of solid-state NMR as a powerful tool for studies of micro- and mesoporous molecular sieves has been dramatic during recent years. Tremendous progress has been made, aiming towards enhanced resolution, sensitivity and improved multinuclear capabilities. Solid-state NMR is nowadays a well established technique for characterization of zeolites and related materials with respect to structure elucidation, catalytic behavior and mobility properties.

Solid-state NMR is a complementary technique to XRD, since both crystalline and amorphous material as well as powders can be investigated. While XRD (preferably on single crystals) provides information about the long range ordering and periodicities, NMR allows investigations on the short range ordering (local environment) and structure.

The potential of high-resolution solid-state NMR has been known for a long time. However, the challenge has always been to overcome the problems in connection with recording solid-state NMR spectra with sufficient resolution. Distinct nuclear spin interactions like chemical shift anisotropy (CSA), dipolar and quadrupolar interactions which lead to excessive line broadening, are averaged in liquids due to fast thermal/molecular motions of molecules, but are operative in the rigid lattice of solids (the molecules are less mobile). As a consequence, the fine structure is lost since broad lines are obtained, hiding the essential information of analytical character. In addition, long spin-lattice relaxation times, due to the lack of translation- and rotation-motions, are controlling the repetition of a NMR experiment and, consequently, the entire recording time. During recent years, several techniques have been developed for averaging those interactions / phenomena to zero, or reduce them to the isotropic values, allowing the registration of high-resolution NMR spectra of solids as well. Those techniques and their relations to the mentioned interactions / phenomena are:

Techniques	Handling of the following interactions / phenomena
Dipolar decoupling (DD)	Heteronuclear dipolar interactions
Multiple pulse sequences (MPS)	Homonuclear dipolar interactions
Magic angle spinning (MAS)	Chemical shift anisotropy (CSA), dipolar and first-order quadrupolar interactions
Dynamic angle spinning (DAS)	Second-order quadrupolar interactions
Double orientation rotation (DOR) or Multiple-quantum NMR	
Cross polarization (CP)	Long spin-lattice relaxation times

During MAS, the sample is rotated quickly about an angle of $\vartheta = 54°44'$ in relation to the axis of the external magnetic field, and the three interactions mentioned have a dependence on the second-order Legendre polynomial $3\cos^2\vartheta-1$. That means, if ϑ is chosen to be 54°44′ (the so-called magic angle), the expression $3\cos^2\vartheta-1$ becomes equal to zero and the interactions are averaged to zero or reduced to the isotropic values.

Quadrupolar nuclei interact not only with the magnetic field in which the sample is placed but also with the electric field gradient. The combination of both effects results in an anisotropy that can no longer be removed by MAS alone. A detailed analysis of the averaging process of quadrupolar nuclei shows that second-order quadrupolar interactions depend on a fourth-order Legendre polynomial $35\cos^4\vartheta - 30\cos^2\vartheta + 3$. Therefore, the introduction of two independent angles averages the effect of both tensors and high resolution solid-state NMR spectra of nuclei possessing quadrupole moments can be recorded. In principle, two different techniques can be used: Applying DAS, the sample is rotated sequentially about two different angles, whereas during DOR, the sample is spun simultaneously about the two axes. However, using multiple-quantum NMR

spectroscopy the same information can be obtained.

The spinning speed of a rotor during MAS or DAS/DOR experiments should be at least in the range of the line width of the signal recorded under static conditions, otherwise the main resonance line is accompanied by a series of spinning side bands occurring at integral multiples of the spinning speed. Cross polarization (CP) allows transfer of magnetization (or polarization) from an abundant species (usually ^{1}H) to a dilute species which is under observation. The benefits are primarily an intensity enhancement of the dilute spin signal and a reduction of the recycle time between experiments, since the rate-determining relaxation time is now that of the abundant species. Usually the relaxation of the abundant spins are much faster than the dilute spin relaxation. In order to obtain optimum line narrowing and improved sensitivity in a solid-state NMR spectrum, the experimental techniques mentioned are often applied in combination, as, for example, CP/MAS or CRAMPS (combined rotation and multiple pulse spectroscopy).

All of the relevant basic nuclei contributing to the framework of zeolites and $AlPO_4$ molecular sieves are detectable to NMR investigations by their natural isotopes (natural abundance in parentheses): ^{29}Si (4.7%), ^{27}Al (100%), ^{31}P (100%) and ^{17}O (0.037%). Both ^{27}Al and ^{31}P spectra are easily detected within reasonable time, however, ^{27}Al has a quadrupole moment which can cause line broadening due to interaction with the electric field gradient. Investigations of ^{17}O NMR can be done by using enriched material, since the natural abundance is quite low.

The obtained resonance lines for ^{31}P and ^{29}Si are usually narrow, and, due to their important role as framework elements (besides ^{27}Al), these nuclei have been widely used in solid-state NMR studies of microporous and mesoporous molecular sieves for structural investigations. The most important application of ^{29}Si NMR is due to the relationship between the ^{29}Si chemical shift sensitivity and the degree of condensation of the Si-O tetrahedra, that is, the number and type of tetrahedrally coordinated atoms connected to a given SiO_4 unit: Si (n Al), with n = 0, 1, 2, 3 or 4 [chemical shift range: -80 to -115 ppm, with the high-field signal for Si (0 Al)]. Here n indicates the number of Al atoms sharing oxygens with the SiO_4 tetrahedron under consideration. Differences in chemical shifts between Si (n Al) and Si (n+1 Al) are about 5-6 ppm. Furthermore, ^{29}Si MAS NMR spectra can be used to calculate the framework Si / Al ratio from the NMR signal intensities (I) according to eq. (1):

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$$\frac{Si}{Al} = \frac{\sum_{n=0}^{4} I_{Si(n\,Al)}}{\sum_{n=0}^{4} 0.25\, n I_{Si(n\,Al)}} \qquad (1)$$

^{27}Al NMR spectra reveal the existence of extra-framework Al (about 0 ppm) besides the lattice aluminum (tetrahedrally coordinated Al at about 40-65 ppm). However, in special cases aluminum atoms can be "invisible" and are not observable by NMR. The introduction of DAS and DOR as well as nutation NMR (where in a two-dimensional way the effect of the quadrupole interaction is separated from other line broadening interactions) allow a much more detailed insight with respect to the structural information available by ^{27}Al NMR. Usually, the only Al transition recorded in microporous and mesoporous materials is the central $+1/2 \Leftrightarrow -1/2$ transition, which is dependent only on the second order quadrupolar interaction. This interaction decreases with increasing magnetic field strength, and better resolution can be obtained by applying higher magnetic fields and/or DAS/DOR. Both ^{29}Si and ^{27}Al MAS NMR spectra are widely used to follow dealumination processes, as well as direct synthesis procedures concerning ^{29}Si NMR.

Solid-state ^{1}H NMR of protons, OH groups, adsorbed water, organic sorbates and probe molecules containing hydrogen in microporous and mesoporous molecular sieves has been developed as a usable method for getting information about different kinds of hydrogens in terminal or bridging OH groups, varying environments for hydrogen containing probe molecules and, finally, acidity investigations. In this way, four distinct types of protons have been identified and quantified by their chemical shifts: (1) non-acidic, terminal SiOH groups (1.5-2 ppm), (2) AlOH

groups at non-framework Al (2.6-3.6 ppm), (3) acidic, bridging hydroxyl groups SiO(H)Al (3.6-5.6 ppm) and (4) ammonium ions (6.5-7.6 ppm). Cross polarization measurements are used to emphasize signals of nuclei connected to hydrogen containing environments.

Other nuclei which can substitute isomorphously for the usual framework elements in microporous and mesoporous materials are observable by solid-state NMR, for example, ^{11}B, ^{73}Ge and $^{69,71}Ga$. Charge compensating cations, like ^{7}Li, ^{23}Na, ^{39}K, ^{133}Cs or ^{195}Pt, are suitable for NMR measurements. However, most of those elements possess a quadrupole moment which usually limits the application. Furthermore, organic compounds used as templates during hydrothermal synthesis or as sorbates in the zeolite framework (adsorbed guest molecules can cause frame transitions) as well as catalytic organic reactions on microporous and mesoporous molecular sieves (even *in situ*) can be detected by applying ^{13}C CP/MAS NMR.

Finally, ^{129}Xe (natural abundance of 26.4%) is a very suitable and sensitive isotope for probing the pore architecture of zeolites and $AlPO_4$'s. The extended Xe electron cloud is easily deformable due to interactions, for example, the Xe atoms and the channel wall of a zeolite framework. The deformation results in a large low-field shift of the Xe resonance. Probe molecules like water and hydrocarbons have been used to study the pore architecture of mesoporous materials by monitoring the ^{1}H NMR intensity of the liquid water signal when decreasing the temperature. The intensity of the liquid water ^{1}H NMR signal drops drastically when the water is frozen, however, the temperature for this transition depends strongly on the pore diameter of the porous material. A surprising consistency between the nitrogen adsorption-desorption isotherms and the proton NMR signal intensity versus temperature was observed (see Figure 1).

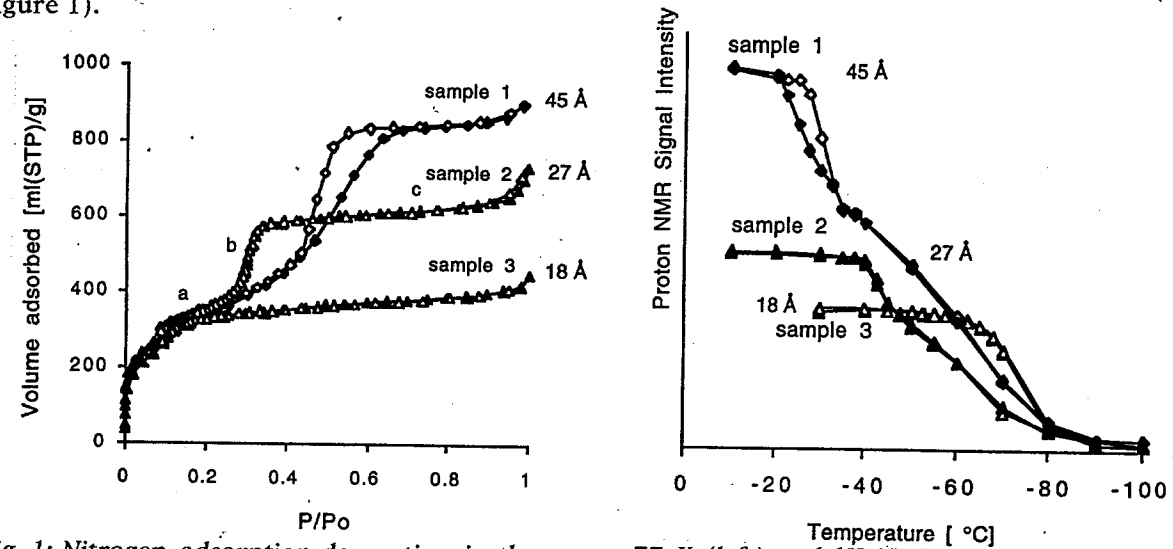

Fig. 1: Nitrogen adsorption-desorption isotherms at 77 K (left) and ^{1}H NMR signal intensities of pore water confined in different siliceous MCM-41 samples versus temperature (right) (pore diameters are given in Å). Filled symbols denote adsorption (left) and cooling (right), open symbols denote desorption (left) and heating (right).

The introduction of two-dimensional (2D) solid-state NMR spectroscopy enables us to follow the three dimensional connectivities within a zeolite lattice (Si-O-Si), by applying 2D homonuclear ^{29}Si COSY (Correlated Spectroscopy) or 2D ^{29}Si INADEQUATE (Incredible Natural Abundance Double Quantum Transfer Experiment) sequences.

The mobility/dynamics of small molecules and the intracrystalline mass transfer in porous materials can be followed by diffusion NMR measurements. Most known is the pulsed field gradient (PFG) technique, where the spins have a state which is spatially dependent upon their location along B, (with pulses of linear gradients of B_0).

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Characterization of zeolites by sorption capacity measurements

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1. Introduction

Sorption capacity measurement provides one of the simplest and most direct ways of characterizing a zeolite sample. However, the information derived from capacity measurement generally provides only an estimate of sample purity and/or evidence of consistency with a known structure, rather than a means of differentiation between different structures.

The adsorption equilibrium isotherm for a microporous adsorbent, such as a zeolite, is of type I form in the Brunauer classification and, in the appropriate temperature range, the isotherm is highly favorable with a well defined saturation limit corresponding to complete filling of the intracrystalline pores. [1] The molecular volume of the adsorbed phase corresponds closely to that of the saturated liquid sorbate at the same temperature so the measured saturation capacity can be easily converted to the specific micropore volume (cm^3/gm) or, knowing the crystal density, to the intracrystalline void fraction. Representative isotherms are shown in Figure 1 (a) and (b), and the calculation of the specific pore volumes is summarized in Table 1.

Table 1. Calculation of specific micropore volumes (Fig. 1)

Figure	System	Temperature (K)	Saturation capacity ($g\ g^{-1}$)	Density of saturated liquid sorbate ($g\ ml^{-1}$)	Specimen micropore volume
1 (a)	O_2/CoY	78	0.324	1.2	0.27
1 (b)	Ar-silicalite	77	0.205	1.42	0.144
1 (c)	N_2-silicalite	77	0.116*	0.81	0.143

*First plateau. Second plateau yields essentially the same pore volume if the density of solid N_2 (1.02 g/mL) is used.

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2. Experimental Technique

Several different techniques may be used to measure the capacity. The essential features of the apparatus used for gravimetric and piezometric measurements are shown in Figure 2. [4]

2.1 Gravimetric Method

In a gravimetric experiment the mass of the sample is measured directly using a microbalance connected to a vacuum line, equipped with a pressure gauge and a system for introducing the sorbate vapor. The sample is first degassed under vacuum at elevated temperature and then cooled to the measurement temperature. Successive doses of sorbate are introduced and the sorbate pressures and corresponding masses are recorded. Provided that the temperatures and range of sorbate pressures are correctly selected, the isotherm should be almost rectangular. Under these conditions accurate measurement of the sorbate pressure is not necessary since the capacity is almost independent of pressure.

2.2 Piezometric Method

In the piezometric method the quantity of sorbate adsorbed is deduced from measurements of the change in pressure in a system of known volume when a known quantity of sorbate is introduced. The system volume can be easily determined using a calibrated doser volume. Accurate

pressure measurements are needed, and of course the entire system should, ideally, be maintained at a uniform constant temperature. This requirement imposes significant practical difficulties when the measurements are to be made at a temperature far from ambient. For this reason the gravimetric method is generally preferred.

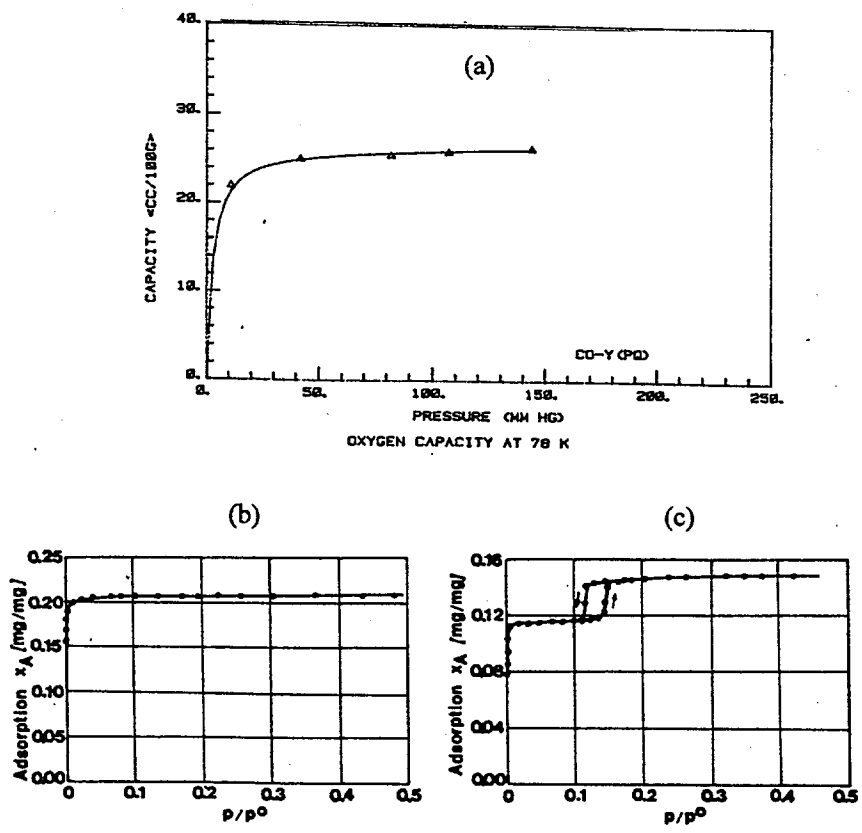

Fig. 1. Experimental isotherms at 77 K: (a) O_2 on CoY [2], (b) Ar on silicalite [3], (c) N_2 on silicalite [same sample as in (b)] [3]

2.3 Automated BET System

Automated BET measurement systems such as *Omnisorb* can also be used to measure saturation capacity. In such devices a dilute stream of sorbate in an inert (He) carrier is passed through the sample and the capacity is found by integration of the measured breakthrough curve, thus providing essentially the same information as is obtained from a gravimetric or piezometric measurement.

Although the basic experiment is very simple, a number of precautions are necessary to obtain accurate results:

(1) In principle a buoyancy correction is needed to allow for the mass of vapor displaced by the zeolite sample. However, except at high pressures, such corrections are generally negligible.

(2) It is important to minimize any temperature gradient in the region of the sample in order to

avoid errors due to thermal transpiration and convection. Thiscan normally be achieved simply by ensuring that the hangdown tube containing the sample pan dips well below the surface of the thermostat liquid.

(3) To avoid the possibility of capillary condensation in the interstices between crystals the sample should be dispersed on the balance pan and the relative pressure (p/p_S) should not exceed about 0.25. (p_S is the saturation vapor pressure at the relevant temperature).

(4) At high relative pressures significant (multilayer) physical adsorption can occur on the external surface of the crystals. If the crystals are small (sub-micron), this can give rise to a significant error in the measured capacity. This problem can also be avoided by keeping the relative pressure below about 0.25.

(5) To correct for the positive slope of the saturation plateau the Dubinin-Radushkevich equation is sometimes used to extrapolate to zero pressure. However, with a near rectangular isotherm of the kind shown in Figure 1, the difference between this extrapolation and the actual value at the plateau is minor.

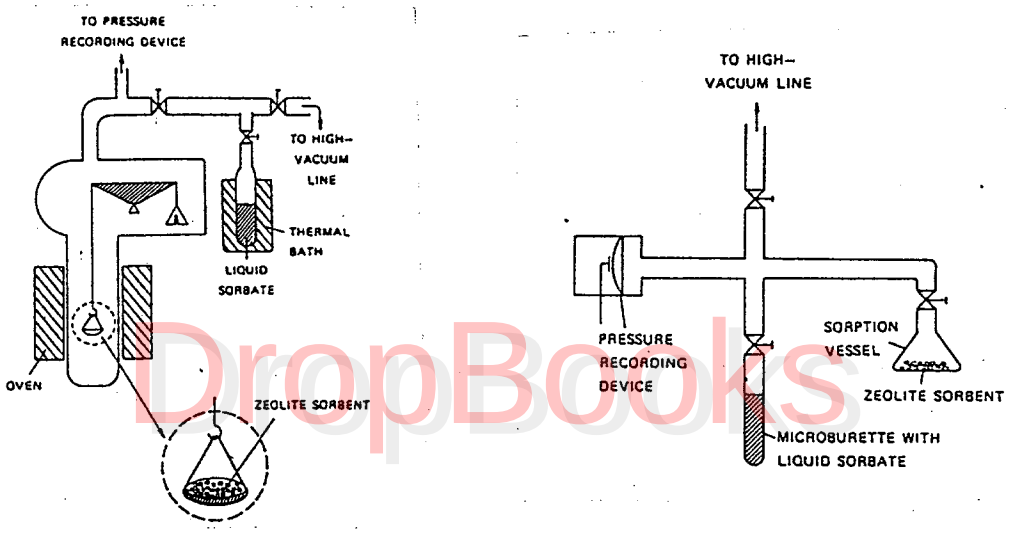

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Figure 2. Schematic diagrams showing apparatus for gravimetric and piezometric isotherm measurements [4]

3. Preconditioning

Prior to a capacity measurement any organic template from the synthesis must be removed by oxidation and the sample must be thoroughly degassed. If the synthesis does not include a template then only the degassing step is needed. Oxidation to remove the template is generally carried out by exposure to air for several hours at the highest temperature that can be tolerated by the zeolite without structural degradation--typically 500-550°C for silicalite/ZSM-5. Degassing is conveniently carried out at elevated temperature in the vacuum system. Temperatures in the range 350-400°C are commonly used, but for less stable materials somewhat lower temperatures can be used. To some extent a reduction in temperature can be compensated for by using a higher vacuum for a longer period of time. The aluminum rich zeolites have poor hydrothermal stability, that is, they are unstable in the presence of water vapor at elevated temperatures. In degassing such samples it is therefore important to raise the temperature slowly maintaining a good vacuum all the time so that water vapor is removed as soon as it is desorbed.

A typical procedure for degassing a sample of A or X zeolite is as follows:

(1) Increase temperature under vacuum from ambient to 400°C over a period of 4-5 hours.

(2) Maintain the temperature at 400°C under vacuum overnight.

(3) Cool (under vacuum) to the experimental temperature (1-2 hours.).

4. Choice of Sorbate and Measurement Temperature

In principle almost any of the common small molecules can be used as the probe sorbate although, in practice, the choice is generally restricted to Ar, O_2 or N_2. Linear paraffins such as n-hexane have sufficient flexibility to pack within the micropores almost as effectively as the smaller molecules so n-hexane capacities are also commonly used to measure specific micropore volume. Bulkier molecules such as i-butane pack less efficiently and thus yield erroneously low estimates for the micropore volume. Molecules such as Ar, O_2 and N_2 do not penetrate 6-membered oxygen rings, at least at low temperatures, so the saturation capacity determined from measurements with these sorbates includes only the pore volume accessible through 8-rings (or larger). Although N_2 is the usual choice of probe molecule for BET surface area measurements, it is not the best choice for measuring the micropore volume of a zeolite, since, probably as a result of quadrupole interactions, N_2 isotherms commonly show complex changes in packing density leading to hysteresis of the isotherm, even for an ideal pore system. [3,5] In contrast, the low temperature isotherms for Ar and O_2 are generally close to the ideal rectangular form (see Fig. 1).

The choice of measurement temperature is dictated by the practical requirement that the desired relative pressure range ($0.05 < p/p_s < 0.2$) should correspond to an easily measured range of absolute pressures. This means that if the measurements are to fall within the convenient subatmospheric pressure range, the temperature should not be too far from the normal boiling point of the sorbate.

Water is a very small molecule, and, as a result of its strong dipole, it is strongly adsorbed, especially in Al-rich zeolites. Water isotherms at ambient temperature generally show the characteristic rectangular form observed for other small molecules. However, the saturation capacities for water (based on the molecular volume) are often higher than the values determined using Ar, O_2 or even N_2 since water can penetrate regions of the framework (for example, sodalite and cancrinite cages) which are not accessible to Ar, O_2 and N_2. Comparison between the saturation capacities measured with water and with Ar, O_2 or N_2 can therefore provide additional structural information.

5. B.E.T. Area

BET areas are commonly determined for zeolite samples by the same method as is used for larger pore materials. [6] Under the conditions of the BET measurement the N_2 molecules condense, filling the micropore volume. Thus the BET area of a zeolite is really the equivalent area that would be covered by the quantity of sorbate required to fill the intracrystalline pores if the molecules were arranged as a close packed monolayer. It does *not* correspond to the internal area of the framework.

6. Mesoporosity

As a result of structural defects the intracrystalline pores of a zeolite sometimes contain a significant proportion of mesopores (20-50 Å) in addition to the ideal zeolite pores (< 15 Å). The presence of significant mesoporosity leads to a positive slope instead of the almost horizontal saturation plateau characteristic of an ideal microporous structure.

7. Determination of Pore Size

In this article we have considered only the use of capacity measurement to determine specific micropore volume. Such measurements using molecules of different critical diameter may also be used to establish the controlling pore dimensions in an unknown structure (see, for example Gaffney, et al., [7]) but this is outside the scope of the present review.

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Ion exchange capacity

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1. Natural Zeolites

In a traditional aluminosilicate zeolite the source of the ion exchange capacity is the extent of isomorphous substitution of Al for Si in the tetrahedral framework. The theoretical exchange capacity thus can be derived from the elemental composition.

To estimate the CEC (cation exchange capacity, meq/g) in a natural zeolite it is usual to observe the uptake of the ammonium cation at room temperature when equilibrium conditions are known to have been attained in the presence of a 1M ammonium salt solution. This working capacity can be obtained by batch or column exchange techniques. [1]

2. Synthetic zeolites and related materials of SAPO, MeAPO type ("zeotypes") [2]

When synthetic materials are to be characterized, prior careful elemental analysis will provide the expected, theoretical cation capacity. It is now important to establish equilibrium conditions with a specific cation for which the synthetic product has a highly selectivity; consider:

$$AZ + B_{aq} = BZ + A_{aq}$$

At equilibrium the "as-synthesized" cation A, in the zeolite phase Z, has been completely displaced by the selective uptake of cation B from the aqueous phase (aq). The following procedure is recommended assuming that the ammonium cation will be the B species.

2.1 Determination of cation exchange capacity at equilibrium.

(1) Weigh suitable aliquots of the zeolite into sealable polyethylene tubes.
(2) Add equal volumes of a known concentration of ammonium nitrate solution to the tubes and mix at room temperature. It is preferable to mix by rolling the tubes slowly about their horizontal axis. Mineralogical rollers of the type used to polish gemstones can easily be adapted for this purpose. The solid/solution volume ratio should be at least 1/20.
(3) At appropriate time intervals remove each tube in turn and determine the concentrations of the displaced cation (A) in solution.
(4) Construct a plot of the concentration in solution of A as a function of time (Fig 1. plot 1). The vertical axis can be expressed as fractional attainment of equilibrium assuming the calculated theoretical capacity as 100%.

2.2 Notes

(a) To quote the capacity in meq/g it will be necessary to determine the equilibrium water capacity of the end member (for example, the B form of the zeolite).
(b) If the expected theoretical capacity is not reached (Fig 1. plot II) it means that, at room temperature, cations in certain sites are not being displaced. This is the ion-sieving phenomenon and can be used to help in structural interpretation of the zeolite structure. Increasing the temperature at which exchange is performed should enable the attainment of full capacity. Usually temperature in the range 60° - 70°C are adequate.
(c) Choice of conditions are a function of the expected theoretical capacity. A "rule of thumb" is to aim for a 5-fold solution excess of ingoing cation (B). The time for attainment of equilibrium depends on the openness of the zeolite framework and will vary from about 1 hour to 1 week.

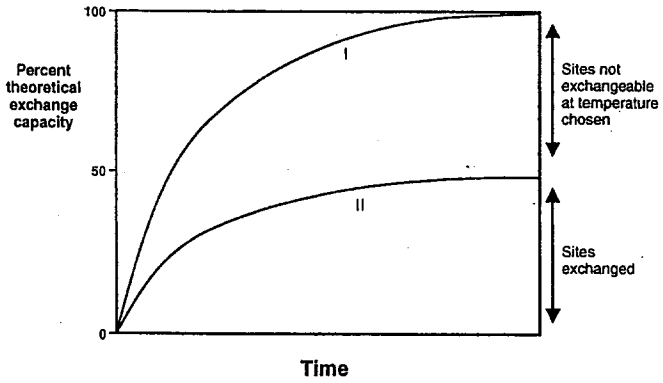

Fig. 1.

3. Experimental methods

The most sensitive analytical technique available is to use radioisotopes to prelabel the A cation and follow its replacement by increase in solution activity with time. (Isotope dilution technique). This will be possible for the as synthesized cations Na, K, Rb, Cs, Ca, Sr and Ba.

In the absence of radiochemical facilities, flame photometry, atomic absorption are perfectly adequate. An alternative is to monitor the ammonium concentration by Kjeldahl titrimetry. Ammonium concentrations can be determined in either the zeolite or solution phase.

4. Other points

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(1) When an organic template has been used to synthesize the zeolite, careful calcination is needed to remove it from the framework. This leaves the zeolite in the H form (H_3O^+ cation in solution). In these cases it is possible to use pH titration to follow ammonium (or other cation) uptake as the H_3O^+ has a low affinity for most zeolites. An exception can be in exchanges observed in materials of SAPO / MeAPO types. These materials sometimes show an unusual affinity for the H_3O^+ ion, especially over Na^+. [3]

(2) It is advisable to limit washing to a minimum. Zeolite frameworks are well known to hydrolyze. This is not confined to just those with Si/Al ratio →1. [4] It is always advisable to check for the presence of extra framework Al (by MAS NMR). This can arise from template removal and from instability of P-containing frameworks. Obviously, extra framework Al contributes to cation exchange capacities, but can be quantified. [5]

(3) Some zeolite like materials and high silica materials may have cation and anion capacities due to the presence of framework hydroxyls. This will be pH dependent, but experience is that these OH groups make small contributions to exchange capacities. [6]

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Characterization by IR spectroscopy

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1. Techniques

The KBr pellet technique is frequently used for investigations of vibrations of the framework. [1-3] Also well-established are (i) infrared (IR) spectroscopy of self-supporting wafers (usually in transmission mode [4]) and (ii) diffusive reflectance IR Fourier transform (DRIFT) spectroscopy of zeolite powders. [5] Both methods (i) and (ii) enable us to investigate cation vibrations in the far IR region [6, 7], to employ heat treatment, to achieve complete dehydration (in high vacuum or a stream of inert gas) and, if desirable, to admit probes (see below). Also, the (thermal) stability of zeolitic materials against, for example, dehydration, dehydroxylation and interaction with sorbates, may be characterized by (*in situ*) transmission IR or DRIFT. In the case of method (i) it is easier to carry out quantitative measurements, while method (ii) is in many instances more sensitive.

2. Framework vibrations

Vibrations of the frameworks of zeolites give rise to typical bands in the mid and far infrared. A distinction is made between external and internal vibrations of the $TO_{4/2}$ tetrahedra (with, for example, T = Si or Al). The original assignments of the main IR bands [1] were as follows: internal tetrahedra: 1250 - 920 cm^{-1}, asymmetrical stretch (n_{asym}); 720 - 650 cm^{-1}, symmetrical stretch (n_{sym}); 500 - 420 cm^{-1}, T-O bend; external linkages: 650 - 500 cm^{-1}, double ring vibrations; 420 - 300 cm^{-1}, pore opening vibrations; 1150 - 1050 cm^{-1}, asymmetrical stretch; 820 - 750 cm^{-1}, symmetrical stretch. The positions of bands due to vibrations of external linkages are often very sensitive to structure. More recent detailed analysis, however, showed that these assignments may have to be revised in some respect. Computation of normal modes suggested that the concept of strictly separated external and internal tetrahedral vibrations must be modified in that zeolite framework vibrations appear to be strongly coupled. Similarly, the proposed pore opening vibrations seem to be related to a complex motion which in total includes an opening (rupture) of the rings (4-rings, 6-rings) of the structure. [2] Nevertheless, clear-cut linear relationships were found between the frequency of, for example, n_{asym} and n_{sym} of X- or Y-type zeolite and the atom fraction of Al (related to the ratio n_{Si}/n_{Al}) of the framework. [1] Thus, the frequencies of lattice vibrations could be used in certain cases to determine the n_{Si}/n_{Al} ratio of the framework in a similar manner as the lattice parameters obtained by X-ray diffraction as a function of this ratio. Also, shifts of the bands of lattice vibrations are characteristic of cation movements upon dehydration. [1] In several cases a typical lattice vibration is observed around 950 cm^{-1}, indicating the isomorphous substitution of framework Si, Al by other T atoms. The most prominent example is Ti substituted for Si into silicalite (TS-1, TS-2). [8]

3. Cation vibrations

In the far infrared region (200 - 50 cm^{-1}) vibrations of cations against the framework occur. [6, 7] The wave number of the corresponding IR bands depend on the nature of the cations as well as on their siting. The IR bands of alkali metal-exchanged zeolites X, Y and ZSM-5 shift to lower frequencies (red shift) in the sequence of Na^+, K^+, Rb^+, Cs^+, that is, with increasing cation mass. [6, 7]

4. Extra-framework species

Extra-framework species such as aluminium-containing entities, (for example $Al_xO_y^{n+}$), which occur upon dehydroxylation, [9] may be detected and quantitatively determined by IR spectroscopy when suitable probe molecules are employed as adsorbates. [10,11] The most frequently used probe is still pyridine. Pyridine attached to Lewis acidic centres such as $Al_xO_y^{n+}$ gives rise to a typical band at about 1450 cm^{-1}. Adsorption of pyridine on cations of zeolite structures produces bands in the range from 1438 to 1452 cm^{-1}. The exact positions of these bands depend on the nature of the cation, that is, on the Coulomb potential q/r (q: electric charge; r: radius of the respective cation). [10] In cases where the pyridine molecule is too bulky to have access to the extra-framework species, smaller probe molecules such as NH_3, CO, CH_3CN, H_2, N_2 can be used advantageously. [5,11,12]

5. Hydroxyl groups

Hydroxyl groups attached to zeolite structures are most important for the chemistry of these materials. They may be detected and characterized by IR spectroscopy as such due to their vibration modes (OH fundamental, overtone and combination vibrations) or with the help of probe molecules (see preceding paragraph and Refs. [5, 11, 12]). A distinction is made among (i) lattice termination silanol groups, (ii) hydroxyl groups occurring at defect sites (hydroxyl nests), (iii) OH-groups attached to extra-framework T atom-containing species (iv) OH groups attached to multivalent cations which compensate the negative charge of the framework and, most importantly, (v) bridging OH-groups (such as ≡Al (OH) Si≡ groups with Brønsted acidic character). Hydroxyls of type (i), (ii), (iii), (iv) and (v) give rise to bands in the fundamental stretch region at about 3740, 3720, 3680, 3580 - 3520 and 3600 - 3650 cm^{-1} (free bridging OH-groups), respectively. Bridging OH-groups exhibiting additional electrostatic interactions to adjacent oxygens are indicated by lower wavenumbers, for example, at *ca.* 3550 cm^{-1} in the case of the hydrogen forms of faujasite type (X and Y) zeolites and at 3520 cm^{-1} in the case of H-ZSM-5. Moreover, the fundamental stretching vibrations of free bridging OH-groups, which are responsible for important catalytic properties of the hydrogen forms of zeolites, depend on the nature of the T atoms in the ≡T(OH)Si≡ configuration. It is, for instance, frequently observed that the respective wavenumbers decrease in the sequence T = Al, Ga, Fe, B. [13] From the intensity (integrated absorbance) of the bands being typical of the above-mentioned types of hydroxyls, the density (concentration) of the corresponding entities can be estimated. To obtain the absolute data the appropriate extinction coefficients must be determined through independent measurements. [14] This is particularly valuable in the case of defect sites and acid Brønsted (bridging) OH groups. Similarly, there seems to exist a correlation between the wave number indicative of bridging OH groups of zeolites and their acidic strength. [15]

Investigation of the overtone and combination vibrations of hydroxyls *via* DRIFT spectroscopy is a valuable means for characterization of zeolite materials since it frequently reveals more detailed features than are obtained from the fundamental stretch region. [16]

Adsorption of probes such as ammonia, pyridine or less basic molecules (such as benzene, CO, alkanes, $C_2Cl_4H_2$, N_2, etc.) also enables zeolitic OH-groups, especially acidic Brønsted sites, to be characterized. Pyridine, for instance, produces a band around 1540 cm^{-1} when adsorbed on Brønsted acid sites, resulting in the formation of pyridinium ions. In view of the bulkiness of pyridine and its strong basicity (low selectivity with respect to acidic strength of the Brønsted sites), other probes should sometimes be preferred. Finally, it should be mentioned that Lewis and Brønsted acidity of zeolites is often advantageously characterized by a combination of IR spectroscopy and other techniques such as temperature-programmed desorption or microcalorimetric measurements of adsorbed probe molecules.

DropBooks

6. Adsorbates

IR spectroscopy is extensively used to characterize zeolite/adsorbate systems. Adsorption and desorption of water (hydration and dehydration) may be easily monitored by IR, since adsorbed H_2O gives rise to a typical deformation band around 1640 cm^{-1}. Adsorbed or occluded template molecules (or their decomposition products) are detectable by, for example, CH and/or NH vibration bands.

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How to read a patent

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Patents contain information useful in zeolite synthesis, but they are hard to read. So why read them? Because they are often the first and sometimes the only source of this information. Much of it is eventually published in the open literature with the arcane language of the patent discarded along the way. But for those on the cutting edge of discovery, the delay may be intolerable. To one "experienced in the art," the inventor discloses more of his/her thought and research than is generally realized. Finally the inventor's summary of the state of the art may be useful to one new to the field.

In reading a patent, it helps to know what to look for and what to ignore. For example, ignore the claims section at the end of the patent. These are lawyers talking to lawyers; rarely is there useful data there. On the other hand, Example 1 usually tells you what works. Pay progressively greater attention to examples where the product has been extensively analyzed and/or used in subsequent applications experiments. Examples which define the limits of operability are warnings for what can go wrong in replicating his/her work. Ignore examples written in the present tense; these are not experiments but the inventor's best guess as to what might happen under hypothetical conditions.

To the beginner, the "state of the art" summary may be a good source of references. The inventor is obliged to cite all pertinent art because failure to do so weakens the case, but the reader should be aware that the inventor is obliged to show that his/her invention is superior to existing art.

"Summary of the invention" may be useful for a long and complex case. At this point, Claim 1 may be a help. Patent attorneys struggle to get the inventor to define exactly what he/she has invented. It helps to be aware of the process by which a patent case is written and prosecuted. The inventor, pushed by the attorney, rushes to assemble the data to support the case and get it filed. The attorney presses the inventor for wide ranging examples to support broad claims. This is the reader's window for discerning the working of the research organization. The case may be refiled during prosecution to delete some of this superfluous and revealing data, but most often it is not. Bad data weakens the case so the inventor is obliged to be truthful about the data, but there is no obligation to present data damaging to the case. This data selectivity makes patents a suspect source in the opinion of many scientists.

DropBooks

Notes

a. Of the aluminosilicate ABW type analogues, only the hydrated Li-form and the anhydrous Rb-, Cs-, and Tl-forms may be directly synthesized. [2]
b. Addition of small amounts of potassium fluoride are reported to have a marked mineralizing effect. [3]
c. In a gold-lined steel autoclave, the reaction was performed at 285°C in 72 hours.
d. Good results have been obtained by crystallization at 200°C for 93 hours.
e. At temperatures above 350°C α-eucriptite is formed. Li_2SiO_3 may occur. [1]
f. Upon dehydration of zeolite Li-A(BW) the framework topology is retained, but the 8-ring channel is considerably narrowed. The lithium cation coordinates across the channel, preventing rehydration of the material even when submerged in water. However, by hydrothermal treatment at temperatures above 110°C, rehydration to the original zeolite is possible.
g. The Si/Al ratios of ABW type are close to 1. Though Li-A(BW) may be synthesized from oxide compositions with Si/Al ratios from 0.5 to 7, there is no evidence of variation in the Si/Al ratio of the product. [3]
h. Reversible dehydration of Li-A(BW) is possible to a limited extent. [4] The anhydrous ABW-types do not show any sorption of water at ambient conditions.
i. In one experiment (sodium bromosodalite and LiBr, hydrothermal 260°C, 72 h), single crystals large enough for single crystal diffraction were obtained (0.1 x 0.05 x 0.01 mm) [1,5]

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AEI $AlPO_4$-18 Al(50), P(50)

Contributed by Rune Wendelbo

Verified by S. Kaliaguine, by E. Dumitriu, and by C. Round

Type Material: $[Al_{24}P_{24}O_{96}]$

Method: S. T. Wilson, E. M. Flanigen [1, 2]

Batch Composition: $Al_2O_3 : P_2O_5 : (TEA)_2O : 60\ H_2O : 6\ i\text{-}C_3H_7OH$ (TEA = tetraethylammonium)

Source Materials

distilled water
phosphoric acid (85%)
aluminum isopropoxide (Jansen, 98+ %)
tetraethylammonium hydroxide (Aldrich, 40% (TEA)OH)[a]

Batch Preparation (for 15.8 g dry product)

(1) [36.3 g water + 15.0 g phosphoric acid + 27.2 g aluminum isopropoxide], add diluted phosphoric acid to the aluminum isopropoxide in a 250 mL polypropylene bottle and shake vigorously for one minute
(2) [(1) + 49 g (TEA)OH solution], shake to produce a uniform gel. Transfer to the autoclave

DropBooks

Crystallization

Vessel: 200 mL Teflon-lined stainless steel autoclave (Berghof)
Incubation: 6 hours at room temperature
Time: 69 hours[b]
Temperature: 215°C[b]
Agitation: gentle[c]

Product Recovery

(1) Recover solid product by centrifugation[d]
(2) Wash once with distilled water; recover product by centrifugation[d]
(3) Dry overnight at 100°C
(4) Calcine for 4 h at 550°C in flowing dry air
(5) Store under nitrogen. Yield near 100%

Product Characterization

XRD: fully crystalline AEI; competing phase: AFI[e]
Elemental Analysis: 24.26% Al, 20.59% P, 0.20% Si[f]
Crystal size and habit: square platelets 0.2-8 μm x 0.1 μm thick[g]

References

[1] S. T. Wilson, E. M. Flanigen, US Patent 4 310 440 (1982)
[2] R. Wendelbo, D. Akporiaye, A. Andersen, I. M. Dahl, H. B. Mostad, Appl. Catal. A: General 142 (1996) L197

Notes

a. This product is now traded as 35% (TEA)OH solution. I would use the same volume of the 35% solution, since the synthesis is not sensitive to a variation of the template concentration of this order. It is important that the (TEA)OH source have minimum K^+ and Na^+ concentrations.
b. The synthesis temperature can probably be reduced to 200°C and the time reduced substantially, but this has not been tested.
c. Standing autoclaves in a heated block on a "shaking table" rotated at about 60 rpm.
d. Filtration leads to loss of fine material or goes very slowly depending on the filter.
e. AFI appears as a contaminant.
f. A Cameca microprobe was used averaging 5 points each 50 x 50 μm. The analysis was done on "as synthesized material."
g. Micropore volume 0.28 mL/g (by N_2 adsorption).

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AEI SAPO-18[a] Al(49), P(42), Si(9)

Contributed by Jiesheng Chen and John M. Thomas

Verified by S. Schunk, by J. López Nieto, and by D. Akolekar

Type Material: $[Al_{24}P_{20}Si_4O_{96}] : mR : nH_2O$ (R = N,N-diisopropylethylamine)[b]

Method: J. Chen, P. A. Wright, J. M. Thomas, S. Natarajan, L. Marchese, S. M. Bradley, G. Sankar, C. R. A. Catlow [1]

Batch Composition: $0.40\ SiO_2 : Al_2O_3 : 0.90\ P_2O_5 : 50\ H_2O : 1.60\ R$

Source Materials

distilled water
phosphoric acid (Aldrich, 85% H_3PO_4)
aluminum hydroxide hydrate (Aldrich, ca. 55% Al_2O_3)
Aerosil (Degussa, 99% SiO_2)
N,N-diisopropylethylamine (Aldrich, 99% $C_8H_{19}N$)

Batch Preparation (for ~2 g product)

(1) [19.4 g water + 3.48 g phosphoric acid + 4.64 g aluminum hydroxide hydrate], stir until homogeneous
(2) [(1) + 0.60 g Aerosil], stir until homogeneous
(3) [(2) + 5.10 g N,N-diisopropylethylamine], stir until homogeneous

DropBooks

Crystallization

Vessel: PTFE-lined stainless steel autoclave
Temperature: 160°C
Time: 8 days
Agitation: none

Product Recovery

(1) Filter; wash with distilled water
(2) Dry at 50°C in air
(3) Yield: 60% based on Al_2O_3

Product Characterization

XRD: [c] Characteristic strong reflections at d = 9.1 and 5.1 Å for as-synthesized materials; competing phase is AFI when $P_2O_5/Al_2O_3 > 1.2$ or $R/P_2O_5 < 1.2$

Elemental Analysis (exclusive of R and H_2O): $0.35\ SiO_2 : Al_2O_3 : 0.87\ P_2O_5$

Crystal Size and Habit: small cubes less than 2 μm in diameter [d]

References

[1] J. Chen, P. A. Wright, J. M. Thomas, S. Natarajan, L. Marchese, S. M. Bradley, G. Sankar, C. R. A. Catlow, J. Phys. Chem. 98 (1994) 10216
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Notes

a. Preparation for SAPO-18 only is given. For AlPO4-18 [2], no Aerosil is added, and the amounts of reactants should be changed to give gel composition $Al_2O_3 : P_2O_5 : 50\ H_2O : 1.80\ R$

b. $AlPO_4$-18 was originally prepared by using tetraethylammonium hydroxide (TEA-OH) as the template in the presence of HCl. It is not possible to prepare SAPO-18 using (TEA)-OH. [3, 4]

c. The XRD patterns of the AEI materials are very sensitive to water molecules present in the channels of the structure.

d Crystals are typically cubic; crystal size increases to a certain degree as the amount of silica in the reaction mixture increases.

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AEI SAPO-18[a] P(50), Al(48), Si(02)

Contributed by Rune Wendelbo

Verified by E. Dumitriu and by C. Round

Type Material: $[Al_{23.2}Si_{0.8}P_{24}O_{96}]$[b]

Method: R. Wendelbo, D. Akporiaye, A. Andersen, I. M. Dahl, H. B. Mostad [1]

Batch Composition: Al_2O_3 : 0.98 P_2O_5 : 0.015 HCl : 0.075 SiO_2 : $(TEA)_2O$: 70 H_2O : 2.8 i-C_3H_7OH[c]
(TEA = tetraethylammonium)

Source Materials
distilled water
aluminum isopropoxide (Jansen, 98+%)
phosphoric acid (85%)
hydrochloric acid (37%)
silica sol (DuPont Ludox LS-30, 30% SiO_2)
tetraethylammonium hydroxide (Aldrich, 40 % (TEA)OH)[d]

Batch Preparation: (for 13.8 g dry product)
(1) [108 g water + 81.6 g aluminum isopropoxide], mix in a one liter poly-propylene bottle and shake for 1 minute
(2) [1) + 45 g phosphoric acid], shake for 1 minute then cool under running tap water
(3) [(2) + 0.6 g hydrochloric acid], shake bottle[e]
(4) [(3) + 3.0 g silica sol], shake bottle. filter gel for 10 minutes (water suction). About 100 g filtrate is removed and discarded. Transfer one-third of filter cake gel to a 250 mL plastic bottle
(5) [One-third (4) + 49 g tetraethylammonium hydroxide solution], shake

DropBooks

Crystallization
Vessel: 200 mL stainless steel, Teflon-lined autoclave (Berghof)
Incubation: 12 hours at room temperature
Time: 120 hours
Temp: 215°C
Agitation: gentle[f]

Product Recovery
(1) Recover solid product by centrifugation.[g]
(2) Wash once with distilled water; recover product by centrifugation[g]
(3) Dry overnight at 100°C
(4) Calcine for 4 hours at 550°C in flowing, dry air
(5) Store under nitrogen. Yield near 100%

Product Characterization
XRD: fully crystalline AEI; competing phase AFI and CHA[h]
Elemental Analyses: 0.84% Si, 19.9% Al, 26.6% P[i]
Crystal size and habit: square platelets, 0.1-2.0 μm x 0.1 μm thick[j]

Reference

[1] R. Wendelbo, D. Akporiaye, A. Andersen, I. M Dahl, H. B. Mostad, Appl. Catal. A: General 142 (1996) L197

Notes

a. Mg APO-18 and Zn APO-18 were synthesized like SAPO-18 by using Mg and Zn nitrates in place of colloidal silica in equivalent amounts on a molar basis. The Mg and Zn nitrates were dissolved in the phosphoric acid 20 m prior to mixing with the other reagents. Products showed 0.14 Mg and 0.10 Zn (mmol/g).
b. Based on Si content; excess P is unexplained.
c. It is assumed that water, HCl and isopropanol are lost in equal proportions and no other components are lost in gel filtration.
d. This product is now traded as 35% (TEA)OH solution. I would use the same volume of the 35% solution, since the synthesis is not sensitive to a variation of the template concentration of this order. It is important that the (TEA)OH source have minimum K^+ and Na^+ concentrations.
e. Addition of HCl has previously been found to allow better control of Si substitution in SAPO-34 and has been used in this case for the same purpose.
f. Standing autoclaves in a heated block on a "shaking table" rotated at about 60 rpm.
g. Filtration leads to loss of fine material or goes very slowly depending on the filter.
h. At lower water content, AFI appears as a contaminant; at higher water content, CHA appears.
i. Analysis by XRF.
j. Micropore volume 0.25 mL/g (by N_2 sorption)

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AEL $AlPO_4$-11 Al(50), P(50)

Contributed by Kristin Vinje

Verified by J. Campelo and by J. Kornatowski

Type Material: $[Al_{20}P_{20}O_{80}] : wH_2O$

Method: R. Szostak, B. Duncan, R. Aiello, A. Nastro, K. Vinje, K. P. Lillerud [1]

Batch Composition: 1.0 Al_2O_3 : 1.25 P_2O_5 : 2.37 DPA : 1.80 HF : 156 H_2O (DPA = di-n-propylamine)

Source Materials

deionized water
aluminum hydroxide (Aldrich 23918-6, 50-57.5% Al_2O_3)[a]
phosphoric acid (Fisher, 85% H_3PO_4)
di-n-propylamine (DPA)(Kodak, ~ 100%)
hydrofluoric acid (Fisher, 48% HF)

Batch Preparation (for 4 g dry product)

(1) [20.0 g water + 7.8 g aluminum hydroxide] stir well
(2) [(1) + 14.4 g phosphoric acid]; add acid dropwise and stir until effervescence is completed
(3) [(2) + 100 g water]; dilute and stir
(4) [(3) + 12.0 g DPA]; add amine dropwise and stir
(5) [(4) + 10.0 g water 3.75 g hydrofluoric acid]: stir for two hours [b]

DropBooks

Crystallization

Vessel: Teflon-lined steel autoclave
Temperature: 145°C
Time: 18 hours
Agitation: none

Product Recovery

(1) Cool autoclave rapidly.
(2) Filter immediately to recover solids and wash.
(3) Dry overnight at room temperature.
(4) Yield: ~ 70% [c]

Product Characterization

XRD: AEL only crystalline phase: no other crystalline phases or amorphous material detected
Elemental Analysis: (atomic %): 15.5 Al, 13.9 P, Al/P = 1.1[d]
Crystal Habit: Bow-tie crystals constructed of long needles) or needles ~1 mm long)[c]

Reference

[1] R. Szostak, B. Duncan, R. Aiello, A. Nastro, K. Vinje, K. P. Lillerud, in Synthesis of Microporous Materials, M. Occelli, H. Robson, (eds.), Van Nostrand Reinhold, New York (1992), pp 240-7

Notes

a. Consistently good results have been obtained using the Aldrich Al-source, but difficulties were encountered using other aluminum sources.
b. Should produce a clear solution; initial pH = 5.5, final pH = 6.0
c. After 18 hours the yield increases to 50-75% at the expense of the crystal size with smaller 5 to 10 μm crystals resulting.
d. Determined on a CAMECA SX 100 Microbeam

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AFI $AlPO_4$-5 Al(50), P(50)

Contributed by Juergen Caro and Irina Girnus

Verified by S. Cresswell, by B. Weckhuysen, and by G. Schulz-Ekloff

Type Material: $Al_{12}P_{12}O_{48}$

Method: I. Girnus, K. Jancke, R. Vetter, J. Richter-Mendau, J. Caro [1][a]

Batch Composition: Al_2O_3 : 1.3 P_2O_5 : 1.6 TEA : 1.3 HF : 425 H_2O : 6 C_3H_7OH [b]

Source Materials

deionized water
orthophosphoric acid (Merck, 85 wt% H_3PO_4)
triethylamine (TriEA), (Riedel de Häen, $(C_2H_5)_3N$)[c]
aluminum triisopropylate (Merck, $Al(C_3H_7O)_3$)[d]
hydrofluoric acid (Merck, 40 wt% HF in water)

Batch Preparation (for ~ 3 g product)

(1) [7 g water + 3.84 g of phosphoric acid], mix
(2) [(1) + 2.07 g TriEA], add TriEA dropwise and mix
(3) [(2) + 5.23 g aluminum isopropylate], add in small amounts at 0°C with intense stirring then stir the mixture at room temperature for 2 hours
(4) [(0.83 g hydrofluoric acid + 89.2 g water], mix
(5) [(3) + (4)], stir for 2 hours

DropBooks

Crystallization

Vessel: 150 mL Teflon-lined steel autoclaves[e]
Temperature: 180°C (preheated oven)
Time: 6 hours [f]
Agitation: none

Product Recovery

(1) Decant the supernatant liquid and discard
(2) Wash the precipitate four times with 100 mL deionized water
(3) Calcine in air at 600°C until product is colorless (white)[g]
(4) Yield: near 100% on Al_2O_3

Product Characterization

XRD: Characteristic strong reflections at d = 11.90, 5.93, 4.48, 4.24, 3.96, and 3.42Å; competing phases (if present): tridymite
Elemental Analysis: 42.9 wt% P_2O_5, 30.5 wt% Al_2O_3 (P/Al = 1.00)
Crystal size and Habit: Hexagonal columns up to 50 μm [h]

References

[1] I. Girnus, K. Jancke, R. Vetter, J. Richter-Mendau, J. Caro, Zeolites 15 (1995) 33
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[8] I. Girnus, K. Hoffmann, F. Marlow, G. Döring, J. Caro, Micropor. Mater. 2 (1994) 537

Notes

a. The decisive difference of this synthesis from that of Wilson and Flanigen [2,3] is the use of HF as proposed by Kessler and Guth [4]. However, crystallization proceeds also in the absence of HF, but less favorably.
b. Because Al triisopropylate is used as Al source, a fixed amount of 3 isopropyl alcohol molecules per Al is always present in the gel.
c. The $AlPO_4$-5 phase can be prepared with numerous templates. Good results are also reported using tripropylamine [3-5].
d. Other Al sources as pseudoboehmite [2, 3] and Al hydroxide [6] also give good and large crystals.
e. For microwave heating, full Teflon autoclaves.
f. For microwave oven (heating rate 4 grd/sec), 15 minutes at 180°C.g If the product remains brown or gray after 4 hours at 600°C, this can be taken as a hint that free diffusion in the one-dimensional pores is blocked (by stacking faults or by non-framework material) thus preventing oxygen from entering and oxidation products from leaving the pores. By going to 900°C, the material can be make "white," but the uptake capacity remains low.
h. Crystals up to 50 μm in length in the direction of the hexagonal columns are easily obtained; in optimized synthesis, Crystals up to 500 μm are observed. Incorporation of Si [7] or Co [8] gives larger and better crystals. Numerous compositional variants are known.

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Verified Syntheses of Zeolitic Materials. H. Robson, editor

AFI SAPO-5 Al(49), P(35), Si(16)

Contributed by David Young

Verified by R. Borade and by S. Schunk

Type Material: $[Al_{11.8}P_{9.4}Si_{3.8}O_{48}] : rR : wH_2O$

Method: D. Young, M. E. Davis [1][a]

Batch Composition: 0.15 cHA : 0.25 $[(CH_3)_2CHO]_3Al$: 0.25 H_3PO_4 : 13 H_2O : 0.5 SiO_2

Source Materials

deionized water
aluminum isopropoxide (Aldrich, 98+%)
phosphoric acid (Aldrich A.C.S. grade, 85% H_3PO_4)
cyclohexylamine (cHA)(Aldrich, 99+%)
silica sol (Dupont Ludox AS-40, 40% SiO_2)

Batch Preparation (for 1 g product)[b]

(1) [4 g water + 1.44 g aluminum isopropoxide]; make slurry
(2) [1.2 g water + 0.81 g phosphoric acid]; mix
(3) [(1) + (2)]; add diluted phosphoric acid dropwise to the aluminum isopropoxide slurry. Stir and age the gel for one hour to ensure homogeneity
(4) [(3) + 0.42 g cHA]; add cHA dropwise. A viscous gel results. Stir and age for 90 minutes
(5) [(4) + 2.13 g silica sol]; check to see that gel (4) is homogeneous, then add silica sol and stir for 10 minutes [c]

Crystallization

Vessel: 15 mL Teflon-lined autoclave [d]
Temperature: 200°C [e]
Time: 3 hours [f]
Agitation: none

Product Recovery

(1) Remove reactor from the oven and quench cool
(2) Transfer product from the liner to a beaker with a wash bottle [g]
(3) Slurry with 50 mL deionized water. Allow the SAPO-5 crystallites to settle and decant off the suspended impurities. Repeat twice
(4) Filter off product on a Buechner funnel. Wash copiously with water. Air dry
(5) Yield: 1 g (Approximately 85% with respect to phosphoric acid)

Product Characterization

XRD: high purity SAPO-5 free from amorphous or crystalline impurities (SAPO-44)[d]
Elemental Analysis: $Al_{0.49}P_{0.35}Si_{0.16}O_2$[h]
Crystal size and habit: spherical or hexagonal aggregates, average size of 20 μm

References

[1] D. Young, M. E. Davis, Zeolites 11 (1991) 277
[2] S. T. Wilson, B. M. Lok, E. M. Flanigen, US Patent 4 310 440 (1982)
[3] J. A. Martens, C. Janssens, P. J. Grobet, H. K. Beyer, P. A. Jacobs, Stud. Surf. Sci. Catal. 49A (1989) 215

Notes

a. Developed from S. T. Wilson, et al., [2] and from J. A. Martens, et al., [3]
b. When handling small quantities of polar liquids, the use of glassware which has been pretreated with dichlorodimethylsilane is recommended. This ensures a clean transfer of reagents.
c. Failure to mix the reagents in this order will result in different products, i.e., the silicoaluminophosphate analogue of quartz/berlinite.
d. Due to the rapid crystallization of the SAPO-5 product and its propensity to transform to SAPO-44 upon synthesis over-run, small reactors with a narrow aspect ratio are recommended. This synthesis is recommended for a 15 mL capacity reactor. It can be scaled up, but the gel should be split between small reactors. Even with 45 mL reactors, impure product will result.
e. Place autoclave on a rack in a forced convection oven at 200°C.
f. A four hour synthesis time results in SAPO-44 impurities: a two hour reaction yields an amorphous gel. Deliberate over-run of one week will yield an excellent SAPO-44.
g. The pH of the synthesis mother liquor will peak at close to 10, which coincides with the crystallization of the SAPO-5.
h This indicates that the main mode of T-atom substitution is silicon for phosphorous. However, surface analysis reveals significant silicon enrichment with strong evidence for silica islanding by Si-O-Si substitution for Al-O-P. ^{29}Si NMR: P-substitution peak at -90 ppm and Si-O-Si peak at -110 ppm.

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Verified Syntheses of Zeolitic Materials. H. Robson, editor

AFI — CoAPO-5 — P(51), Al(45), Co(4)

Contributed by Myriam Uytterhoeven and An Verberckmoes

Verified by S. Ashtekar, by P. Norby, by J. Jänchen, and by H. van Breukelen

Type Material: $[CoAl_{11}P_{12}O_{48}] : wH_2O$ (w = 0.1 to 0.2)

Method: M. G. Uytterhoeven, R. A. Schoonheydt [1, 2]

Batch Composition: 0.7 TriEA : $(Co_{0.08}Al_{0.92}P)O_4$: 20 H_2O

Source Materials

water (doubly distilled)
phosphoric acid (Janssen Chimica, 85% H_3PO_2)
cobalt nitrate, $Co(NO_3)_2 \cdot 6\ H_2O$ (Janssen Chimica)
pseudoboehmite (Catapal, Vista, 70% Al_2O_3)
triethylamine (TriEA) (Janssen Chimica 99%)

Batch Preparation (for 27 g product)

(1) [62.6 g water + 23.06 g phosphoric acid], mix; chill to 0°C
(2) [(1) + 4.66 g cobalt nitrate], stir until dissolved
(3) [(2) + 13.4 g pseudoboehmite], add alumina under continuous stirring
(4) [(3) + 14.3 g TriEA], add amine under continuous stirring;[a] stir for one additional hour.
Initial pH ≈ 3

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Crystallization

Vessel: stirred, Teflon-lined autoclave
Temperature: 200°C
Time: 24 hours
Agitation: Stirring is essential.[b] Autoclaves were "tumbled" (end-over-end) in the oven

Product Recovery

(1) Filter and wash with distilled water; dry at room temperature
(2) Yield: near 100% on T-atom basis

Product Characterization

XRD: pure AFI, CHA impurity when present is evidenced by a line at 9.5°(2θ)[c]
Elemental Analysis: 0.10 TriEA · $(Co_{0.086}Al_{0.892}P_{1.000}O_4)$ · 0.13 H_2O[d]
Crystal Size and Habit: agglomerates formed by hexagonal platelets, regularly shaped (spherical or diabolo-shaped) with dia. = 55μm[e,f]

References

[1] M. G. Uytterhoeven, R. A. Schoonheydt, Micropor. Mater. 3 (1994) 265
[2] M. G. Uytterhoeven, R. A. Schoonheydt, Proc. Ninth Int. Zeo. Conf., R. von Ballmoos, J. B. Higgins, M. M. J. Treacy (eds.), Butterworth-Heinemann, Boston, 1993, p. 329

Notes

a. TriEA addition causes an exothermic reaction; the preparation should be performed at 0°C and TriEA added drop by drop under careful temperature control.
b. Under static conditions, co-crystallization of CHA is more probable.
c. The co-crystallization of CHA can be suppressed by reducing the amine content and/or decreasing the cobalt content. The latter requires an increase of the Al content so that [Al + Co = P].
d. On T-atom basis, the product composition is almost equal to the gel composition. Al + Co = P should be approximately achieved.
e. SEM is suited to distinguish between AFI and much smaller CHA crystals.
f. At low cobalt content (e.g., $Co_{0.02}Al_{0.98}P_{1.00}$), single crystals are formed, shaped as hexagonal bars. Twinning can occur. Increasing cobalt content causes agglomeration giving larger, regular agglomerates. At high cobalt content (for example, $Co_{0.08}Al_{0.92}P_{1.00}$) single crystal formation can be achieved by increasing dilution and increasing template content, although the latter favors the co-crystallization of CHA.

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AFI SSZ-24 Si(100)

Contributed by S. I. Zones and L. T. Yuen

Verified by A. Bell and C. Gittleman, by A. Cheetham, and by R. Lobo and D. Shantz

Type Material: $(SiO_2)_{24} \cdot aRN^+$ $a = 0.96 \pm 0.24$ (RN^+ = trimethyl-1-adamantammonium)

Method: R. A. Van Nordstrand, D. S. Santilli, S. I. Zones [1]

Batch Composition: 5 K_2O : 15 RN+ : 100 SiO_2 : 4400 H_2O

Source Materials

deionized water

RN^+ (see above) 0.72 Molar [2]
potassium hydroxide (Baker reagent, 87.8% KOH)
fumed silica (Cab-O-Sil M5, 97% SiO_2, 3% H_2O)

Batch Preparation (for 3.5 g product)

(1) [38.32 g water + 13.90 g (0.72M RN+) + 0.44 g potassium hydroxide], mix until dissolved
(2) [(1) + 4.00 g fumed silica], mix in the Teflon liner of a 125 mL Parr stainless steel reactor [a]

Crystallization

Vessel: Parr 125 mL reactor (Teflon-lined) heated in a Blue M oven
Temperature: 150°C
Time: 7 days [b,c]
Agitation: none

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Product Recovery

(1) Upon cooling to room temperature, the product should be settled to the bottom of the reactor liner; pH with a calibrated probe should be 11.50-11.70
(2) Filter to recover solids (medium grade glass-frit funnel)
(3) Wash product with approximately 100 mL 0.01N KOH solution [d]
(4) Wash with approximately 1 liter water
(5) Air dry overnight while pulling a vacuum through the frit
(6) Yield: 3.52 g; 79% yield based on SiO_2

Product Characterization

XRD: AFI only crystalline phase

Elemental Analysis: RN^+ is approximately 10 wt% and alkali cation is usually less than 0.5 wt%. The remaining material is SiO_2 [3]

Crystal Size and Habit: Typically hexagonal rods composed of identical hexagonal plates on top of each other. The rods are usually about 10 μm long

References

[1] R. A. Van Nordstrand, D. S. Santilli, S. I. Zones in Molecular Sieve Science, ACS Symp. Ser. 368, W. H. Flank, T. E. Whyte, (eds.), Am. Chem. Soc., Washington, D. C., 1988, pp. 236-245
[2] S. I. Zones, US Patent 4 665 110 (1987)
[3] I. Petrovic, A. Navrotsky, M. E. Davis, S. I. Zones, Chem. Mater. 5 (1993) 1805
[4] R. A. Van Nordstrand, D. S. Santilli, S. I. Zones, in Synthesis of Microporous Materials, Vol. 1, M. L. Occelli, H. E. Robson (eds.), Van Nostrand Reinhold, New York, 1992. pp. 373-383

Notes

a. High speed stirring of this preparation leads to SSZ-23 formation [1].
b. The reaction can be accelerated by seeding after some initial material has been made.
c. The synthesis of the borosilicate [4] requires only one day; the crystals are smaller.
d. The alkaline wash helps to prevent unreacted silica from coming out of solution during washing and causing pore-plugging.

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AFO SAPO-41 Al(51),P(46).Si(3)

Contributed by A. M. Prakash and D. K. Chakrabarty

Verified by P. Mériaudeau and by J. Pérez-Pariente and J. Rodríguez

Type material: $[(Al_{20.4}P_{18.4}Si_{1.2})O_{80}] \cdot mR \cdot nH_2O$ (R = Di-n-propylamine)

Method: A. M. Prakash, S. V. V. Chilukuri, R. P. Bagwe, S. Ashtekar, D. K. Chakrabarty [1]

Batch Composition: 1.0 Al_2O_3 : 1.3 P_2O_5 : 0.1 SiO_2[a] : 4.0 R[b] : 58.2 H_2O[c]

Source Materials

deionized water
orthophosphoric acid (Merck, 85%)
pseudoboehmite (Vista; Catapal-B, assumed 70 wt% Al_2O_3)
fumed silica (Degussa, Aerosil-200)
di-n-propylamine (Merck, 99%)

Batch Preparation (for ~ 16 g product)

(1) [23.06 g phosphoric acid + 25 g water], mix together
(2) [(1) + 14.57 g pseudoboehmite], add slowly over a period of 3.5 hours and continue stirring for 1.5 hours
(3) [0.60 g silica + 25 g water], mix together to form a slurry
(4) [(2) + (3)], add silica slurry over a period of 30 minutes and continue stirring for 1 hour
(5) [(4) + 40 g water], mix together
(6) [(5) + 40.88 g di-n-propylamine], add dropwise to gel and continue stirring for 30 minutes
(7) Adjust pH of the gel to 7.7 by slowly adding 4 mL of phosphoric acid diluted in 6 g water and stir the final gel for 30 minutes to ensure homogeneity

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Crystallization

Vessel: 500 mL stainless steel autoclave
Temperature: 180°C
Time: 11 days

Product Recovery

(1) Decant the mother liquor
(2) Slurry with deionized water. Allow the crystallites to settle and decant the water
(3) Repeat step (2) three times
(4) Filter off product and wash again with water
(5) Dry at 100°C overnight
(6) Yield: ~ 65% based on alumina

Product characterization

XRD: SAPO-41 [1][d] Orthorhombic; a = 9.7 Å, b = 25.5 Å, c = 8.4 Å; competing phases: SAPO-11 and SAPO-31 at low template concentration and SAPO-46 at high silica concentration [1, 2]
Elemental Analysis (exclusive of R and H_2O): 1.00 Al_2O_3 : 0.90 P_2O_5 : 0.11 SiO_2
Crystal size and habit: 5-10 μm crystals of rectangular morphology

References

[1] A. M. Prakash, S. V. V. Chilukuri, R. B. Bagwe, S. Ashtekar, D. K. Chakrabarty, Micropor.. Mater. 6 (1996), 89

[2] P. Mériaudeau, V. A. Tuan, V. T. Nghiem, S. Y. Lai, L. Hung, C. Naccache, J. Catal. 169 (1997) 55

Notes

a. In this synthesis pure phase SAPO-41 crystallizes only at low SiO_2 concentration in the gel. High concentration of silica generally leads to phases such as SAPO-11, SAPO-31, SAPO-46 depending on template concentration, temperature and period of crystallization.

b. Template concentration should be high (3 mol < R < 4 mol) for obtaining pure SAPO-41. Lower template concentration leads to SAPO-11 and SAPO-31 depending on silica concentration.

c. H_2O included water from pseudoboehmite, phosphoric acid and added water.

d. Extra low-intensity lines between 9-18 degrees (2ϑ) have not been identified. They may indicate a lower symmetry due to retained template. However a competing phase cannot be ruled out.

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AFS MAPO-46 P(50), Al(40), Mg(10)

Contributed by Deepak B. Akolekar

Verified by H. Tian and by A. Prakash

Type Material: $Mg_{5.54}Al_{22.4}P_{28.06}O_{112} \cdot 8.1\ R \cdot 11.0\ H_2O$ (R = di-n-propylamine)

Method: D. B. Akolekar, S. Kaliaguine [1]

Batch Composition: 2 R : 0.30 MgO : 0.85 Al_2O_3 : 1.0 P_2O_5 : 50 H_2O

Source Materials

deionized water
orthophosphoric acid (85%, Aldrich)
pseudoboehmite (Vista Chemical Co., 71.8% Al_2O_3)
magnesium oxide (99.9%, Aldrich)
n-dipropylamine (99%, Aldrich, 0.738 g/mL)

Batch Preparation (for 20 g dry, template-free product)

(1) [65.0 g water + 25.16 g o-phosphoric acid + 13.18 g pseudo-boehmite], stir until homogeneous
(2) [(1) + 1.32 g magnesium oxide + 32.0 g water], stir until homogeneous
(3) [(2) + 29.9 mL n-dipropylamine], stir until homogeneous (about 35 minutes) [a]

Crystallization

Vessel: PTFE-lined stainless steel autoclave (200 mL)
Temperature: 162°C
Time: 240 hours
Agitation: none

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Product Recovery

(1) Stir the total crystallization batch into 1.5 L deionized water. Allow to stand for a few minutes, then decant the top organic layer
(2) Filter; wash with deionized water
(3) Dry at 75°C
(4) Yield: > 60% based on Al_2O_3

Product Characterization

XRD: AFS, only crystalline product [2-4]; characteristic strong reflections at d = 11.43 and 4.12Å
Elemental Analysis (H_2O and template-free): 0.396 MgO · 0.80 Al_2O_3 · 1.00 P_2O_5
Crystal Size and Habit: hexagonal rod-like, 0.8 x 8 μm

References

[1] D. B. Akolekar, S. K. Kaliaguine, J. Chem. Soc., Faraday Trans. 89 (1998) 4141
[2] S. T. Wilson, E. M. Flanigen in ACS Symp. Ser. 398, M. L. Occelli, H. E. Robson (eds.), Am. Chem. Soc., Washington, D.C., 1989, p. 329
[3] E. M. Flanigen, R. L. Patton, S. T. Wilson, Stud. Surf. Sci. Catal. 37 (1988) 13
[4] J. M. Bennett, B. K. Marcus, Stud. Surf. Sci. Catal. 37 (1988) 269

Note

a. Uniform homogeneous gel formation is the important step for obtaining pure phase material.

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ANA Analcime Si(68), Al(32)

Contributed by B. W. Garney

Verified by N. Evmiridis and by F. Farzaneh

Type Material: $Na_x[Al_xSi_{48-x}O_{96}] : 16\ H_2O$ (x = 15 to 17)

Method: Developed from J. F. Charnell [1], and A. Dyer, A. M. Yusof [2]

Batch Composition: $4.5\ Na_2O : Al_2O_3 : 4.5\ SiO_2 : 3.0\ H_2SO_4 : 380\ H_2O : 6.1$ triethanolamine [a]

Source Materials

demineralized water
aluminum sulfate [General Purpose Reagent, $Al_2(SO_4)_3 \cdot 16\ H_2O$]
sodium metaasilicate (Technical Grade, $Na_2SiO_3 \cdot 5\ H_2O$)
triethanolamine [General Purpose Reagent, $N(C_2H_4OH)_3$]

Batch Preparation (for approximately 7 g product) [3,4]

(1) [55 g water + 9.8 g aluminum sulfate], stir until dissolved; filter through 0.7 micron glass microfibre filter
(2) [36.5 g water + 14.9 g sodium metasilicate + 12.2 g triethanolamine], stir until dissolved; filter through 0.7 micron glass microfibre filter
(3) [(1) + (2)], stir gently until gel thickens (do not over-stir)

Crystallization

Vessel: 150 mL Teflon-lined autoclave [b]
Time: 24 hours
Temperature: 200°C (autoclave heated in the oven)
Agitation: none

Product Recovery

(1) Cool to room temperature and filter to recover solids
(2) Wash with distilled water until pH of filtrate < 10
(3) De-agglomerate by adding 10 mL of 10% ethanol in water and immerse in a 150 watt ultrasonic bath for approximately 1 hour
(4) Dry at 100°C
(5) Yield: approximately 90%

Product Characterization

XRD: ANA (only crystalline phase)
Elemental Analysis: $1.06\ Na_2O : Al_2O_3 : 4.3\ SiO_2 : 2\ H_2O$
H_2O (Wt. loss at 500°C): 8.29% (± 0.20)
Na_2O: 14.6% (± 1.5)
Al_2O_3: 22.7% (± 1.5)
SiO_2: 57.3% (± 0.5)
Crystal Size and Habit: polycrystalline non-porous spherulites ≤180 μm dia. [2]

References

[1] J. F. Charnell, J. Cryst. Growth 8 (1971) 291
[2] A. Dyer, A. M. Yusof, Zeolites 7 (1987) 191
[3] B. W. Garney, Fusion Technology 21 (1992) 604
[4] B. W. Garney, UK Patent Application 9011151.9

Notes

a. This preparation gives the non-porous form of analcime. Replacing aluminum sulfate with an equivalent weight of sodium aluminate gives the porous form of analcime. Gel composition: 6.5 Na_2O : Al_2O_3 : 4.5 SiO_2 : 380 H_2O : 6.1 triethanolamine.

b. The method of heating the gel is very important if large crystals are required. The largest crystals were obtained when the autoclave was placed in a laboratory oven where the heat flow was uniform all around the pot. Experiments using autoclaves which were heated by electrical jackets around the sides were not so successful.

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AST $AlPO_4$-16 Al(50), P(50)

Contributed by Joël Patarin

Verified by J. Shi and K. Balkus, by D. Akporiaye, and by T. Blasco

Type Material: $(Al_{10}P_{10}O_{40})Q_{2.0}F_{1.6} : 3.0\ H_2O$[a] (Q = quinuclidine)

Method: C. Schott-Darie, J. Patarin, P. Y. Le Goff, H. Kessler and E. Benazzi [1]

Batch Composition: $1\ P_2O_5 : 1\ Al_2O_3 : 1\ Q : 1\ HF : 60\ H_2O$

Source Materials
- distilled water
- phosphoric acid (Fluka, 85% H_3PO_4)
- aluminum isopropoxide (Aldrich, 98%)
- quinuclidine $C_7H_{13}N$ (Fluka, 97%)
- hydrofluoric acid (Prolabo, 40%)

Batch Preparation[b] (for 1.5 g of as-synthesized product)
(1) [4.00 g water + 2.31 g phosphoric acid + 4.17 g aluminum isopropoxide], stir until homogenized [c]
(2) [6.15 g water + 1.14 g quinuclidine], stir until dissolved
(3) [(1) + (2) + 0.50 g hydrofluoric acid], stir for 2 minutes. Gel pH = 7 to 7.5

Crystallization
- Vessel: Teflon-lined stainless steel autoclave (50 cm^3)
- Temperature: 150°C
- Time: 24 hours
- Agitation: none
- Final pH: approximately 8

Product Recovery
(1) Dilute the reaction mixture with distilled water
(2) Filter or centrifuge
(3) Wash until the pH of the filtrate is 5.5 to 6
(4) Dry at 60-70°C overnight
(5) Yield: 50% based on aluminum (as-synthesized product containing quinuclidine and some water) [d]

Product Characterization
- XRD: AST (only crystalline phase), Space group I4, a_o = 9.3423(1) Å c_o = 13.4760(2) Å[e]
- Elemental Analysis (wt%): Al_2O_3 = 32.8, P_2O_5 = 44.8, F = 1.9, $(C_7H_{13})N$ = 15.4, H_2O = 3.4
- Crystal Size and Habit: tetrahedra, 0.5 to 3 μm

References

[1] C. Schott-Darie, J. Patarin, P. Y. Le Goff, H. Kessler, E. Benazzi, Micropor. Mater. 3 (1994) 123
[2] J. M. Bennett, R. M. Kirchner, Zeolites 11 (1991) 502

Notes

a. The Q/F molar ratio is lower than 1. Part of the quinuclidine is either not protonated or OH^- groups are present in order to get a neutral material.
b. The starting mixture is prepared in a polyethylene vessel.
c. The reaction is exothermic.
d. After calcination (removal of the organic and fluoride species) the cubic form [2] of $AlPO_4$-16 is obtained.
e. According to reference [1].

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ATN MAPO-39 P(50), Al(40), Mg(9)

Contributed by Deepak Akolekar

Verified by P. Norby and by S. Sivasanker

Type Material: $H_{1.6}[Mg_{1.6}Al_{6.4}P_8O_{32}]$

Method: D. B. Akolekar, S. K. Kaliaguine [1]

Batch Composition: 1.1 R : 0.40 MgO : 0.80 Al_2O_3 : 1.00 P_2O_5 : 41 H_2O (R = di-n-propylamine)

Source Materials

deionized water
orthophosphoric acid (85%, Aldrich)
pseudoboehmite (Vista Chemical Co., 71.8% Al_2O_3)
magnesium oxide (99.9%, Aldrich)
n-dipropylamine (99%, Aldrich, 0.738 g/mL)

Batch Preparation (for 12 g dry, template-free product)

(1) [70.0 g water + 32.3 g o-phosphoric acid + 15.91 g pseudoboehmite], stir until homogeneous
(2) [(1) + 2.26 g magnesium oxide + 26 g water], stir until homogeneous
(3) [(2) + 19.2 mL n-dipropylamine], stir until homogeneous (about 30 minutes) [a]

Crystallization

Vessel: PTFE-lined stainless steel autoclave (150 mL)
Temperature: 150°C
Time: 114 hours
Agitation: none

Product Recovery

(1) Stir the total crystallization batch into 1.5 L deionized water
(2) Filter; wash with deionized water
(3) Dry at 75°C
(4) Yield: > 70% based on Al_2O_3

Product Characterization

XRD: ATN [2,3], characteristic strong reflections at d = 4.19 and 3.95Å for as-synthesized material
Elemental Analysis: (exclusive of R and H_2O) (wt%): 6.31 MgO, 34.32 Al_2O_3, 59.37% P_2O_5
Crystal Size and Habit: small irregular platelike particles, 2.5 x 3.3 μm

References

[1] D. B. Akolekar, S. K. Kaliaguine, Zeolites 14 (1994), 620
[2] S. T. Wilson, E. M. Flanigen, in ACS Symp. Ser. 398, M. L. Occelli, H. E. Robson (eds.) Am. Chem. Soc., Washington, D.C., 1989, p. 329
[3] L. B. McCusker, G. O. Brunner, A. F. Ojo, Acta Crystallogr. A46 (1990), C 59

Note

a. Uniform homogeneous gel formation is the important step for obtaining pure phase material.

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BEA Zeolite Beta Si(93), Al(7)

Contributed by Joaquin Pérez-Pariente and Miguel Camblor

Verified by Shu-Hua Chien and Xianping Meng, and by D. Cardoso and S. Jahn

Type Material: $Na_{0.92}K_{0.62}(TEA)_{7.6}[Al_{4.53}Si_{59.47}O_{128}]$[a]

Method: M. A. Camblor, J. Pérez-Pariente [1]

Batch Composition: 1.97 Na_2O : 1.00 K_2O : 12.5 $(TEA)_2O$: Al_2O_3 : 50 SiO_2 : 750 H_2O : 2.9 HCl[b]

Source Materials

deionized water
tetraethylammonium hydroxide (Alfa 40 wt% TEAOH, K < 1 ppm, Na < 3 ppm)
sodium chloride (reagent grade)
potassium chloride (reagent grade)
silica (Degussa Aerosil 200, 99+% SiO_2)
sodium hydroxide (Prolabo reagent grade, 98%)
sodium aluminate (Carlo Erba, 56 wt% Al_2O_3, 37 wt% Na_2O)

Batch Preparation (for 20 g product)

(1) [59.4 g water + 89.6 g TEAOH (40%) + 0.53 g sodium chloride + 1.44 g potassium chloride], stir until dissolved
(2) [(1) + 29.54 g silica], stir until homogenized (10 minutes minimum)
(3) [20.0 g water + 0.33 g sodium hydroxide + 1.79 g sodium aluminate], stir until dissolved
(4) [(2) + (3)], stir for 10 minutes, (gives a thick gel)

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Crystallization

Vessel: 60 mL stainless steel autoclaves with Teflon liners
Temperature: 135 ± 1°C
Time: 15 to 20 hours
Agitation: autoclaves are rotated (60 rpm)[c]

Product Recovery

(1) Quench autoclaves in cold water, product pH = 12.8 ± 0.1
(2) Centrifuge (10,000 rpm), wash until pH ~ 9 and dry overnight (77°C)
(3) Yield: 9.9 ± 0.2 g of solid / 100 g gel (~ 90% on Al)

Product Characterization

XRD: zeolite beta (no other phases)
Elemental Analysis (content per unit cell): $Na_{0.90}K_{0.62}(TEA)_{7.6}[Al_{4.53}Si_{59.47}O_{128}]$[d]
(Si/Al = 13.1±0.1)
Crystal Size and Habit: The crystals are round-shaped. They do not show any particular crystal habit. Average crystal size is 0.20 μm, and the crystal size distribution is very narrow. (The size of ~90% of crystals is between 0.10-0.30 μm)

References

[1] M. A. Camblor, J. Pérez-Pariente, Zeolites 11 (1991) 202
[2] M. A. Camblor, A. Mifsud, J. Pérez-Pariente, Zeolites 11 (1991) 792

Notes

a. Highly siliceous beta (Si/Al~ 100 can be obtained by using tetraethyl-orthosilicate as silica source [2].
b. $OH^-/SiO_2 = 0.56$
c. In the specific synthesis conditions given in the recipe, the agitation has practically no influence on the properties of the product. However, by using different synthesis conditions, large differences in total crystallization time, average crystal size and crystal size distribution can be found between static and agitated synthesis.
d. Excess cations assumed to be occluded TEAOH or TEA+ compensating SiO-structure defects.

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BEA [Ti,Al] Beta Si(95), Ti(3), Al(2)

Contributed by Dilson Cardoso

Verified by M. Camblor and by W. S. Ahn

Type Material: $(TEA)_{1.5}[Ti_{2.0}Al_{1.5}Si_{60.5}O_{128}]$ (TEA = tetraethylammonium)

Method; S. Jahn, D. Cardoso [1,3], M. A. Camblor, A. Corma, J. Pérez-Pariente [2]

Batch Composition: 0.033 TiO_2 : SiO_2 : 0.0026 Al_2O_3 : 0.269 $(TEA)_2O$: 15.5 H_2O

Source Materials

tetraethylammonium hydroxide (Aldrich, 35% TEA-OH aqueous solution)
tetraethylorthotitanate (Aldrich, 99%)
silica (Degussa Aerosil 380, 99+%)
aluminum nitrate ($Al(NO_3)_3 \cdot 9\ H_2O$)
deionized water

Batch Preparation (for ~1 g product)

(1) [13.24 g tetraethylammonium hydroxide solution + 0.44 g tetraethylortho-titanate], mix in a glove box; stir for 10 minutes[a]
(2) [(1) + 3.52 g silica], stir for 15 minutes
(3) [0.11 g aluminum nitrate + 7.69 g water], stir until dissolved
(4) [(3) + (2)], stir until homogenized (10 minutes minimum)[b]

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Crystallization

Vessel: 50 mL stainless steel autoclave with Teflon liner
Time: 60-96 hours
Temperature: 140°C
Agitation: optional
Final pH: ~12.5

Product Recovery

(1) Quench autoclave in cold water
(2) Centrifuge (7000 rpm) and wash until pH is about 9 [c]
(3) Dry overnight at 80°C
(4) Yield: 3-4 g/100 g batch (about 90% based on Al, 40% on Ti and 25% on Si)

Product Characterization

XRD: zeolite beta (no other phases)
Elemental analyses: $Ti_{2.0}Al_{1.5}Si_{60.5}O_{128}$ (for material with 96 hours crystallization. As synthesized material contains TEA+ cations)
Crystal size and habit: round-shaped particles with average size 0.28 μm (for 96 hours crystallization) and a narrow size distribution

References

[1] S. L. Jahn, P. A. P. Nascente, D. Cardoso, Zeolites 19 (1997) 416
[2] M. A. Camblor, A. Corma, J. Pérez-Pariente, Zeolites 13 (1993) 82
[3] S. L. Jahn, D. Cardoso, in Proceedings of 12th International Zeolite Conference, Vol. III, M. M. J. Treacy, B. K. Marcus, M. E. Bisher, J. B. Higgins (eds.), Materials Research Soc., Warrendale, PA, USA (1998), pp 1885-1892,

Notes

a Tetraethylorthotitanate hydrolyses very rapidly under normal atmospheric conditions forming extra framework TiO_2. Using this Ti-source, the gel must be prepared in a glove box. If this equipment is not available, the gel can be prepared under normal atmosphere using a solution of tetraethylortho-titanate in isopropyl alcohol (TEOTi/iPrOH molar ratio of 1/10). This results in a small loss in solid yield.

b. It is difficult to synthesize the beta structure in total absence of aluminum. This recipe employs the minimum content of this element (Si/Al ~400).

c. The solid particles formed during synthesis are very small, and it is very difficult to filter them. Unfortunately the appropriate method for purification is by centrifugation.

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CAN Cancrinite Si(50), Al(50)

Contributed by J.-Ch. Buhl

Verified by C. Williams and by M. Bottale

Type Material: $Na_8[AlSiO_4]_6CO_3 \cdot 4H_2O$

Method: J.-Ch. Buhl [1]

Batch Composition: 93 Na_2O : Al_2O_3 : 2 SiO_2 : 10 $NaHCO_3$: 1386 H_2O[a]

Source Materials

distilled water
sodium hydroxide (Merck pellets, analytical grade)
kaolin (Fluka)
sodium bicarbonate (Merck, analytical grade, $NaHCO_3$)

Batch Preparation (for 0.6 g product)

(1) [45 mL water + 14.4 g sodium hydroxide], stir until dissolved
(2) [(1) + 0.5 g kaolin + 1.7 g sodium bicarbonate], mix until uniform slurry

Crystallization

Vessel: Teflon-lined steel autoclave
Temperature: 200°C
Time: 48 hours
Agitation: none

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Product Recovery

(1) Cool to ambient temperature. Filter
(2) Wash free of NaOH residuals (approximately 150 mL water)
(3) Dry at 80°C
(4) Yield: close to 100%

Product Characterization

XRD: CAN; small amounts of a disordered phase between CAN and SOD and amorphous material could be detected in the polycrystalline sample [1,2]
Elemental Analysis: $Na_8[AlSiO_4]_6CO_3 \cdot 4H_2O$[b]

Crystal Size and Habit: small elongated needles [c]

References

[1] J.-Ch. Buhl, Thermochimica Acta 178 (1991) 19
[2] G. Hermeler, J.-Ch. Buhl, W. Hoffmann, Catalysis Today 8 (1991) 415
[3] C. Liu, S. Li, K. Tu, R. Xu, J. Chem. Soc., Chem. Commun. (1993) 1645

Notes

a. CAN-formation in the water-free system is reported using butane-1,3-diol. [3]
b. Analysis of the guest anions according to the combination of simultaneous thermal analysis (TG, DTG, DTA), IR-spectroscopy and MAS NMR (^{13}C).
c. Single crystals can be prepared from a gel consisting of [50 mg kaolin (heated at 1400°C for two hours) + 168 mg $NaHCO_3$ + 320 mg NaOH + 1 mL distilled water] treated at 500°C for 48 hours in a silver-lined steel autoclave.

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CHA Chabazite Si(68), Al(32)

Contributed by Thomas R. Gaffney

Verified by J. Warzywoda, by J. Cejka, and by Liu Xinjin

Type Material: $K_{11}[Al_{11}Si_{25}O_{72}]:40\ H_2O$

Method: M. Bourgogne, J.-L. Guth, R. Wey [1]

Batch Composition: 0.17 Na_2O : 2.0 K_2O : Al_2O_3 : 5.18 SiO_2 : 224 H_2O

Source Materials

demineralized water
potassium hydroxide (J. T. Baker reagent grade, 45% KOH solution)
(Na,H) Zeolite Y (UOP LZY-64)[a]

Batch Preparation (for 25 g dry product)

(1) [198.2 mL water + 26.8 mL KOH (45% solution), mix
(2) [(1) + 25.0 g Zeolite Y], seal in a polypropylene bottle and shake for 30 s

Crystallization

Vessel: polypropylene bottle with a screw-top lid
Temperature: 95°C (steam chamber)
Time: 96 hours
Agitation: none

Product Recovery

(1) Remove bottle from the steam chamber and filter to recover solids while still hot [b]
(2) Wash two times with 500 mL water per wash
(3) Dry at ambient temperature [c]
(4) Yield: 99% based on alumina, 83% based on silica

Product Characterization

XRD: CHA with no reflections from FAU. Competing phases; FAU when insufficient crystallization times are used [d]

Elemental Analysis: 0.02 Na_2O : 0.98 K_2O : Al_2O_3 : 4.32 SiO_2 (dry basis)[e,f]

Crystal Size and Habit: Sub-micron crystallites, 0.1 μm on average, multifaceted (some can be seen to be hexagonal platelets)

Reference

[1] M. Bourgogne, J.-L. Guth, R. Wey, US Patent 4 503 024 (1985)

Notes

a. The Na/Al ratio of the NaHY starting materials should be less than 0.17. LZY-64 was prepared by heating NH_4^+ exchanged type Y to 550°C (at 2°C/minute) and calcining at 550°C for 2 hours. Caution: ammonia is liberated during the calcination. Use adequate ventilation and safety precautions.

b. pH = 13.5 after crystallization treatment.

c. The product is stable to drying in an oven at 110°C.

d. Converting samples of Zeolite Y which contain large crystals or are formed (pelleted, beaded) to chabazite requires longer reaction times.

e. The framework SiO_2/Al_2O_3 is 4.32 by ^{29}Si NMR.

f. For preparing more siliceous product, Nalco 2326 silica (14.5% SiO_2) was used as the silica source. Synthetic chabazite with SiO_2/Al_2O_3 = 5.3 forms from a reaction mixture of composition: 0.17 Na_2O : 4.31 K_2O : Al_2O_3 : 8 SiO_2 : 500 H_2O. Addition of more silica to the reaction mixture (batch SiO_2 : Al_2O_3 > 8) leads to incomplete conversion of Zeolite Y, and the product is a mixture of CHA and FAU.

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CHA SSZ-13 Si(93), Al(7)

Contributed by L. T. Yuen and S. I. Zones

Verified by R. Lobo and by L. Schreyeck

Type Material: (aRN, bNa) $[Al_{2.4}Si_{33.6}O_{72}] : wH_2O$[a] (w = 1 to 7)
(RN = N,N,N, trimethyl-1-adamantammonium)

Method: S. I. Zones, R. A. Van Nordstrand [1]

Batch Composition: 10 Na_2O : 2.5 Al_2O_3 : 100 SiO_2 : 4400 H_2O : 20 RN-OH

Source Materials
sodium hydroxide (1N), (Baker, reagent grade)
N,N,N, trimethyl-1-adamantammonium hydroxide (RN-OH)(0.72M)[b]
deionized water
aluminum hydroxide (Reheis F-2000 dried gel, 50% Al_2O_3)
fumed silica (Cab-O-Sil, M5 grade, 97% SiO_2)

Batch Preparation (for 0.6 g product)
(1) [2.00 g 1N NaOH + 2.78 g 0.72 M RN·OH + 3.22 water], add sequentially to the Teflon cup of a Parr 23 mL autoclave [c]
(2) [(1) + 0.05 g aluminum hydroxide], mix until solution clears
(3) [(2) + 0.60 g fumed silica], mix until uniform

Crystallization
Vessel: Teflon-lined 23 mL autoclave (Parr model 4745)
Temperature: 160°C [d]
Time: 4 days
Agitation: none

Product Recovery
(1) Cool to room temperature [e]
(2) Filter in a medium frit glass funnel
(3) Wash with about one liter of water
(4) Air dry at room temperature with vacuum pulling through frit
(5) Yield: 0.57 g, 74% based on TO_2

Product Characterization
XRD: CHA (only crystalline phase); competing phases when observed: analcime or quartz; impurities can occur at this temperature or higher.
Elemental Analyses: RN is approximately 15 wt% and SiO_2/Al_2O_3 = 28 by ICP
Crystal Size and Habit: cubes of 2-5 μm with some occasional intergrowth

References

[1] S. I. Zones, R. A. Van Nordstrand, Zeolites 8 (1988) 166
[2] S. I. Zones, US Patent 4 544 538 (1985)
[3] S. I. Zones, Trans. Faraday Soc. 87 (1991) 3709

Notes

a. Typical values: a = 1.4 to 2.9, b = 0.7 to 4.3
b. The description of template preparation is given in [2]. The fastest synthesis of this product is from FAU sources [3].
c. The Teflon cup is washed between runs with HF (48%), water, KOH solution, and water again.
d. The reactor is placed into a Blue M convection-heating oven preset at 160°C.
e. pH of the treated batch should measure in the range of 12.20 to 12.64 using a calibrated probe

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CHA SAPO-34 Al(47), P(32), Si(21)

Contributed by A. M. Prakash

Verified by J. López Nieto and by N. Tusar

Type Material: $mR[Al_{17}P_{12}Si_7O_{72}]$ (R = morpholine)

Method: A. M. Prakash, S. Unnikrishnan [1]

Batch Composition: $Al_2O_3 : 1.06\ P_2O_5 : 1.08\ SiO_2 : 2.09\ R : 66\ H_2O$[a,b]

Source Materials

distilled water
phosphoric acid (Merck, 85%)
pseudoboehmite (Vista Catapal-B, 70% Al_2O_3)
fumed silica (Degussa Aerosil-200 99+% SiO_2)
morpholine (Aldrich, 99% C_4H_9O)

Batch Preparation(for 20 g product)[c]

(1) [18.0 g water + 15.37 g phosphoric acid], mix
(2) [(1) + 9.20 g pseudoboehmite], add slowly (2 hours) with stirring
(3) [(2) + 10 g water], stir thoroughly for 7 hours
(4) [4.09 g fumed silica + 11.62 g morpholine + 15 g water], mix thoroughly
(5) [(3) + (4)], add (4) dropwise to (3) while stirring
(6) [(5) + 24 g water], stir thoroughly for 7 hours; pH of gel = 6.4 to 7.5

Crystallization

Vessel: 150 mL Teflon-lined autoclave
Incubation: 24 hours at 38°C without agitation[d]
Temperature: 200°C
Time: 24 hours
Agitation: none

Product Recovery

(1) Decant the mother liquor
(2) Dilute with distilled water and filter
(3) Wash 3 to 4 times with distilled water
(4) Dry at 100°C for 6 hours
(6) Yield: 98% based on alumina

Product Characterization

XRD: SAPO-34 (CHA) [1], a_o = 13.78 Å, c_o = 14.85 Å; competing phase: $AlPO_4$ (crystobalite) when silica and/or template concentration is low
Elemental Analysis: $1.0\ Al_2O_3 : 0.68\ P_2O_5 : 0.87\ SiO_2 : 0.59\ R : 1.07H_2O$
Crystal size and habit: 5 to 20 μm crystals with cubic-like rhombohedral morphology [1]

Reference

[1] A. M. Prakash, S. Unnikrishnan, J. Chem. Soc. Faraday Trans. 90 (1994) 2291

Notes

a. H_2O includes water from phosphoric acid, pseudoboehmite and added water.

b. Concentration of SiO_2 and organic template can vary over a range without affecting the phase purity. At low concentration of silica ($SiO_2/Al_2O_3 \leq 0.3$) or template ($R/Al_2O_3 \leq 1.5$), however, dense phase $AlPO_4$-crystobalite co-crystallizes with SAPO-34.

c. Use Teflon or stainless steel equipment throughout.

d. Although SAPO-34 crystallizes without aging, the crystallinity of the resulting product can be improved by aging.

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CHA SAPO-44 Al(48), P(34), Si(18)

Contributed by S. Ashtekar, S. V.V. Chilukuri and D. K.Chakrabarty

Verified by A. Prakash and by He Chang-Qing

Type Material: 5.0 $(C_6H_{11}NH_2)[Si_{6.5}Al_{17.3}P_{12.2}O_{72}] \cdot wH_2O$[a]

Method: S. Ashtekar, S. V.V. Chilukuri, D. K. Chakrabarty [1]

Batch Composition: $Al_2O_3 : 1.0\ P_2O_5 : 1.0\ SiO_2 : 1.9\ R : 63\ H_2O$[b] (R = cyclohexylamine)

Source Materials
- distilled water
- orthophosphoric acid (85% H_3PO_4)
- pseudoboehmite (Catapal-B, Vista, 70% Al_2O_3)
- cyclohexylamine (99+%)
- fumed silica (99+% SiO_2)

Batch Preparation (for ~ 16 g product)
(1) [90 g water + 34.59 g orthophosphoric acid + 21.86 g pseudoboehmite], mix thoroughly
(2) [60 g water + 28.27 g cyclohexylamine + 9 g fumed silica], mix thoroughly
(3) [(1) + (2)], mix thoroughly with vigorous agitation

Crystallization
- Vessel: stainless steel autoclave
- Temperature: 190°C
- Time: 48 hours
- Agitation: none

Product Recovery
(1) Filter and wash with distilled water
(2) Dry at 110°C
(3) Yield near 100% on Al_2O_3

Product Characterization
- XRD: CHA; competing phase: SAPO-5 (when gel $C_6H_{11}NH_2/Al_2O_3$ ratio < 1.9)
- Elemental Analysis: $(Si_{0.18}Al_{0.48}P_{0.34})O_2$[a]
- Crystal Size and Habit: cubical morphology with 10-50 μm diameter [1]

Reference

[1] S. Ashtekar, S. V. V. Chilukuri, D. K. Chakrabarty, J. Phys. Chem. 98 (1994) 4878

Notes

a. Cations assumed to be protonated amine or surface hydroxyl.
b. H_2O includes water from pseudoboehmite and orthophosphoric acid.

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-CLO Cloverite ($GaPO_4$) P(50), Ga(50)

Contributed by Céline Schott-Darie

Verified by S. Bradley, by W. Schmidt, and by R. Fricke

Type Materials: 8{$[Ga_{96}P_{96}O_{372}(OH)_{24}](QF)_{24}(H_2O)_n$} (Q = quinuclidine [1])

Method: A. Merrouche, J. Patarin, H. Kessler, M. Soulard, L. Delmotte, J.-L. Guth, J. F. Joly [2]

Batch Composition: $Ga_2O_3 : P_2O_5 : HF : 80\ H_2O : 6\ Q$[a]

Source Materials

phosphoric acid (Fluka, 85% H_3PO_4)
distilled water
gallium sulfate [$Ga_2(SO_4)_3 \cdot xH_2O$] (Strem Chemicals, wt.% Ga ~ 18][b]
hydrofluoric acid (Fluka, 40% HF)
quinuclidine (Fluka, 97% $C_7H_{13}N$)

Batch Preparation (for 1 g product)

(1) [0.95 g phosphoric acid + 2.2 g H_2O + 3.14 g gallium sulfate hydrate + 2.2 g H_2O] stir until dissolved
(2) [(1) + 0.2 g HF + 2.7 g quinuclidine], mix until uniform. Initial pH = 4 to 4.5

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Crystallization

Vessel: PTFE-lined autoclave
Temperature: 150°C
Time: 24 hours
Agitation: none

Product Recovery

(1) Filter, wash with distilled water, dry at 60°C
(2) Yield: approximately 60% on Ga_2O_3 and P_2O_5

Product Characterization

XRD: Characteristic strong reflections at d = 25.4, 9.1 and 8.5 Å; competing phases are $GaPO_4$-a and $GaPO_4$-b [2] when the starting molar ratio $F/Ga_2O_3 < 0.5$ [3]
Elemental Analysis (anhydrous form): $Q_{0.14}Ga_{0.48}P_{0.52}O_2F_{0.13}$
Crystal Size and Habit: small cubes, less than 1 μm[c]

References

[1] M. Estermann, L. B. McCusker, C. Baerlocher, A. Merrouche, H. Kessler, Nature 352 (1991) 320
[2] A. Merrouche, J. Patarin, H. Kessler, M. Soulard, L. Delmotte, J.-L. Guth, J. F. Joly, Zeolites 12 (1992) 226
[3] J. Patarin, C. Schott-Darie, A. Merrouche, H. Kessler, M. Soulard, L. Delmotte, J.-L. Guth and J. F. Joly in Proceedings from the 9th International Zeolite Conference, R. von Ballmoos, J. B. Higgins and M. J. Treacy (eds), Butterworth-Heinemann, Stoneham, 1992, p. 263

Notes

a. The acceptable range for HF/Ga_2O_3 is 0.75 to 2.

b. Aldrich $Ga_2(SO_4)_3$ acceptable substitute.

c. Crystals are typically cubes with apparent truncatures when large (20 μm or more). Increase in crystal size has been achieved by decreasing the amount of fluoride in the starting mixture to $F/Ga_2O_3 < 0.5$ [3].

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EAB TMA-E Si(74), Al(26)

Contributed by Rosario Aiello and Flaviano Testa

Verified by B. Schoeman and by B. Subotic´

Type Material: $[Na_{6.84}(TMA)_{3.05}]\,[(AlO_2)_{9.25}(SiO_2)_{26.75}] \cdot 17.12\ H_2O$[a] (TMA = tetramethylammonium)

Method: R. Aiello, R. M. Barrer [1]

Batch Composition: $5\ (TMA)_2O : 3\ Na_2O : Al_2O_3 : 15\ SiO_2 : 500\ H_2O$

Source Materials

distilled water
tetramethylammonium hydroxide (Fluka, purum, 25% aqueous solution)
sodium hydroxide (Carlo Erba, pellets, reagent grade, 30% aqueous solution)
alumina (Pfaltz and Bauer, $Al(OH)_3$, 65% Al_2O_3)
silica (Sigma, fumed, 99+% SiO_2)

Batch Preparation (for 1.4 g dry product)

(1) [13.78 g water + 9.10 g tetramethylammonium hydroxide solution + 2.00 g sodium hydroxide solution], mix until dissolved
(2) [(1) + 0.39 g alumina], mix until homogeneous
(3) [(2) + 2.25 g silica], mix thoroughly

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Crystallization

Vessel: Teflon container
Time: 14 days
Temperature: 80 ± 2°C
Agitation: container is rotated

Product Recovery

(1) Filter and wash thoroughly
(2) Dry at ambient temperature
(3) Yield: near 100% on Al_2O_3

Product Characterization

XRD: EAB (only phase observed); competing phase: FAU (trace sometimes present)[b]
Elemental Analyses: $(Na_2O)_{0.74} : ((TMA)_2O)_{0.33}Al_2O_3 \cdot 5.74\ SiO_2$ [c]
Crystal Size and habit: 1-2 μm faceted spherulites [d,e]

Reference

[1] R. Aiello, R. M. Barrer, J. Chem. Soc. A (1970) 1470

Notes

a. Excess cations attributed to SiO^- fragments in the framework.
b. FAU traces were observed from systems with lower TMA/Na ratio and with lower H_2O content.
c. As reported in Ref. [1] for samples obtained both from batches with Na^+/ $(TMA)^+$ = 0.5/0.5 and 0.2/0.8.
d. TMA^+ could not be removed by $NaNO_3$ exchange.
e. By thermal analysis, water is first lost endothermally, followed by exothermal oxidative decomposition of TMA^+.

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EDI — Barrer K-F — Si(50), Al(50)

Contributed by Juliusz Warzywoda

Verified by T. Gier and by M. Sato

Type Material: $K_{10}(Al_{10}Si_{10}O_{40}) : wH_2O$ $(w \sim 8)$

Method: R. M. Barrer, B. M. Munday [1]

Batch composition: 19.9 $K_2O : Al_2O_3 : 2\ SiO_2 : 378\ H_2O$

Source Materials

deionized water
potassium hydroxide (pellets, 85% KOH min.)
kaolin ($\sim Al_2Si_2O_5(OH)_4$)

Batch Preparation (for 0.8 g product)

(1) [18.2 g water + 7.95 g potassium hydroxide]; dissolve KOH pellets in HDPE [a] bottle
(2) [(1) + 0.78 g kaolin]; seal the bottle and shake for 15 seconds [b]

Crystallization

Vessel: HDPE bottle
Temperature: 80°C
Time: 12 days
Agitation: occasional shaking

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Product Recovery

(1) Filter to recover solids
(2) Wash with deionized water until pH of wash water is neutral
(3) Dry at 80°C
(4) Yield: 0.83-0.86 g (dry) (90% on Al or Si)

Product Characterization

XRD: Barrer K-F (no competing phases) [2]
Elemental Analyses: $K_2O \cdot Al_2O_3 \cdot 2\ SiO_2 \cdot 3\ H_2O$ [3]
Crystal Size and Habit: inter-penetrating prismatic crystals, 2 μm or less

References

[1] R. M. Barrer, B. M. Munday, J. Chem. Soc. (A) (1971) 2914
[2] J. D. Sherman in ACS Symp. Series 40, J. R. Katzer (ed.), Am. Chem. Soc., Washington, D. C., 1977, p. 30
[3] R. M. Barrer, J. W. Baynham. J. Chem. Soc. (1956) 2882

Notes

a. High density polyethylene
b. Upon addition of kaolin to the KOH solution, a slowly settling suspension of solids, rather than a homogeneous gel, is formed.

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EDI — Linde Type F — Si(50), Al(50)

Contributed by Juliusz Warzywoda

Verified by T. Gier and by M. Sato

Type Material: $K_{10}(Al_{10}Si_{10}O_{40}) \cdot wH_2O$ ($w \sim 8$)

Method: J. Warzywoda, R. W. Thompson [1]

Batch Composition: 5.26 K_2O : Al_2O_3 : 3 SiO_2 : 94.5 H_2O

Source Materials
deionized water
potassium hydroxide (pellets, 85% KOH min.)
aluminum (wire, 99.999% Al)
silica (Cab-O-Sil M5, amorphous fumed SiO_2)

Batch Preparation (for 4 g product)
(1) [20.0 g water + 9.26 g potassium hydroxide]; dissolve KOH pellets in HDPE [a] bottle. Divide into two equal portions
(2) [First half (1) + 0.719 g aluminum];[b] dissolve the Al wire in half of the KOH solution by heating under reflux in a Teflon flask. Cool, filter and store in a HDPE bottle
(3) [Second half (1) + 2.42 g silica]; dissolve the silica in the remaining KOH solution and heat at 80-95°C in a HDPE bottle. Cool, filter and store in a HDPE bottle[c]
(4) [(2) + (3)]; heat (2) and (3) in HDPE bottles to 80-95°C and mix together.[d] Mix the resulting gel for 1-2 minutes at 1000 rpm with a mechanical stirrer to homogenize it[e]

Crystallization
Vessel: HDPE bottle
Temperature: 95°C
Time: 96 hours
Agitation: static conditions with occasional mixing

Product Recovery
(1) Filter to recover solids
(2) Wash with deionized water until the pH of wash water is neutral
(3) Dry at 80°C
(4) Yield: 4.4 to 4.7 g (near 100% based on Al_2O_3)

Product Characterization
XRD: Linde Type F (ref. [2], Table III, page 35)
Elemental Analyses: K_2O : Al_2O_3 : $2SiO_2$: $3H_2O$ [3]
Crystal size and habit: small submicron prismatic crystals forming 0.5 to 3 μm aggregates

References

[1] J. Warzywoda, R. W. Thompson, Zeolites 11 (1991) 577
[2] J. D. Sherman, in ACS Symp. Series 40, J. R. Katzer (ed.), Am. Chem. Soc., Washington, D.C., 1977, p 30
[3] R. M. Barer, J. W. Baynham, J. Chem. Soc. (1956) 2882

Notes

a. High density polyethylene.
b. The dissolution of aluminum powder in these caustic solutions generates heat and hydrogen and can be somewhat violent.
c. To avoid precipitation of solids from solutions (2) and (3), carry out crystallization immediately after solution preparations is complete.
d. A viscous aluminosilicate gel is formed instantaneously.
e. If no mechanical stirring is used, the gel appears to be very viscous with no visible fluid phase, and homogenization may be difficult. Brief heating of the gel at 95°C will give a fluid phase and hand shaking can be used to homogenize it.

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EMT EMC-2 Si(79), Al(21)

Contributed by Jens Weitkamp

Verified by Kuei-jung Chao and by T. Chatelain

Type Material: $Na_{20}[Al_{20}Si_{76}O_{192}] \cdot (18\text{-crown-6})_4$ [1]

Method: J. Weitkamp, R. Schumacher [1-3]

Batch Composition: 2.2 Na_2O:Al_2O_3 : 10 SiO_2 : 140 H_2O : 0.87 (18-crown-6)

Source Materials
demineralized water
sodium hydroxide (Fluka reagent grade)
sodium aluminate (Riedel-de Haën; 54% Al_2O_3, 41% Na_2O)
crown ether (Fluka 18-crown-6)
silica sol (Bayer AG, VP 4039, 30% SiO_2)

Batch Preparation (for 19 g product)[a]
(1) [39 g water + 6.05 g NaOH solution (50%) + 7.26 g sodium aluminate + 8.81 g (18-crown-6)], dissolve under continuous stirring
(2) [(1) + 77 g silica sol], stir vigorously

Crystallization
Vessel: stainless steel autoclave (150 mL)
Incubation: one day at room temperature
Temperature: 110°C
Time: 12 days
Agitation: none

Product Recovery
(1) Filter and wash extensively with demineralized water
(2) Dry at 120°C for 16 hours
(3) Yield: approximately 19 g (still containing the template and some adsorbed water), 56% based on Al[b]

Product Characterization
XRD: EMT; competing phases: GIS and FAU
Elemental Analyses: SiO_2/Al_2O_3 =7.6 (by AES/ICP and ^{29}MAS NMR) [2]
Crystal Size and Habit: hexagonal, 4-5 μm mean diameter, 0.5 to 1.0 μm thick

References

[1] F. Delprato, L. Delmotte, J.-L. Guth, L. Huve, Zeolites 10 (1990) 546
[2] J. Weitkamp, R. Schumacher, in Proceed. Ninth Int. Zeo. Conf., R. von Ballmoos, J. B. Higgins, M. M. J. Treacy, (eds.), Butterworth-Heinemann, Boston, 1993, p. 353
[3] J. Weitkamp, R. Schumacher, U. Weiß, Chem.-Ing. Tech. 64 (1993) 1109

Notes
a. This synthesis has been successfully scaled-up by a factor of four (yield 69 g).
b. Calcination at 540°C in air for 16 hours removes template.

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EUO [Ga] EU-1 Si(96.5), Ga(3.5)

Contributed by A. N. Kotasthane

Verified by S. Lambert, by H. Kessler, and by T. Loiseau

Type Material: $Na_5[Ga_4Si_{108}O_{224}] : wH_2O$ (w ~ 26)

Method: G. N. Rao, V. P. Shiralkar, A. N. Kotasthane, P. Ratnasamy [1]

Batch Composition: 7.0 Na_2O : Ga_2O_3 : 36.6 SiO_2 : 4.0 R : 5.55 H_2SO_4 : 926 H_2O[a]
(R = hexamethonium dibromide ($C_{12}H_{30}N_2Br_2$))

Source Materials
demineralized water
sodium hydroxide, reagent grade (97%)
silica sol (27.4% SiO_2, 0.5% Na_2O)
sulfuric acid (AR BDH, 98%)
gallium(III)sulfate (Aldrich 99.99%)
hexamethonium bromide monohydrate (HM-Br_2, Aldrich)

Batch Preparation (for 24 g product)
(1) [30.0 g water + 5.41 g sodium hydroxide], mix until dissolved, pH = 13.8 ± 0.2
(2) [81.0 g silica sol + 20 g water], mix until uniform, pH = 9.8 ± 0.2
(3) [(1) + (2)], mix until uniform, pH = 13.6 ± 0.2
(4) [30 g water + 2.6 g sulfuric acid + 4.3 g gallium sulfate], mix until dissolved; heating on hot plate for 15 minutes essential, pH = 0.08± 0.02
(5) [(3) + (4)], add (4) drop-wise to (3) with good mixing
(6) [30 g water + 15.2 g HM-Br_2], mix until dissolved. pH = 7.2 ± 0.2
(7) [(5) + (6)], add (6) to (5) with good mixing. Adjust final batch to pH = 12.6 with 1 M NaOH [b]

Crystallization
Vessel: stainless-steel autoclave (Parr, 300 mL capacity)
Temperature: 170°C
Time: 6 days
Agitation: propeller mixer (250 RPM)

Product Recovery
(1) Cool and filter to recover solids. Slurry pH after crystallization = 10.5 ± 0.2
(2) Wash extensively with demineralized water until filtrate pH < 9
(3) Dry at 110°C for 12 to 15 hours
(4) Yield: approximately 24 g (56% on Ga_2O_3, 79% on SiO_2)

Product Characterization
XRD: Pure EU-1 phase (EUO framework topology) having characteristic strong reflections at d = 4.30, 3.99 and 3.28Å without any impurity phases. On longer crystallization (above 6 days), alpha quartz appears
Elemental Analysis: 92.4% SiO_2, 5.24% Ga_2O_3, 2.36% Na_2O (SiO_2/Ga_2O_3 = 55.0, Na_2O/Ga_2O_3 = 1.36)[c,d]
Crystal Size and Habit: Homogeneously distributed small spheres (2-3 μm)

Reference

[1] G. N. Rao, V. P. Shiralkar, A. N. Kotasthane, P. Ratnasamy, in Synthesis of Microporous Materials, Vol. I, M. L. Occelli, H. E. Robson (eds.), Van Nostrand Reinhold, New York (1992) p 153

Notes

a. Increasing SiO_2/Ga_2O_3 in gel from 35 to 70 and to 110 gives SiO_2/Ga_2O_3 in product of 79 and 100 respectively. For products with SiO_2/Ga_2O_3 greater than 100, the preferred template is equimolar benzyldimethylamine + benzyl chloride. [1]

b. The Na_2O content of the silica source is significant. If gel pH is less than 12.0, it should be adjusted with NaOH solution.

c. By thermal analysis: template burnout 300-700°C (approximately 10% weight loss).

d. By ^{71}Ga MAS NMR: chemical shift ϑ= 170 ppm (Ga_{3+} in tetrahedral environment).

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FAU — Linde Type X — Si(55), Al(45)

Contributed by Hans Lechert and Philip Staelin

Verified by D. Ginter, by E. Basaldella, and by E. Fallabella Sousa-Aguiar

Type Material: $Na_{86}Al_{86}Si_{106}O_{384} : wH_2O$ (w ~ 260)

Method: H. Lechert, H. Kacirek [1, 2]

Batch Composition: $NaAlO_2 : 4\ SiO_2 : 16\ NaOH : 325\ H_2O$[a,b]

Source Materials

distilled water
sodium hydroxide (99+% NaOH)
alumina trihydrate (Merck, 65% Al_2O_3)[c]
sodium silicate solution (27.35% SiO_2, 8.30% Na_2O, 1.37 g/mL)

Batch Preparation (for 42 g product)

(1) [100 g water + 100 g sodium hydroxide], stir until dissolved
(2) [(1) + 97.5 g alumina trihydrate], stir at 100°C until dissolved, cool to 25°C
(3) [(2) + 202.5 g water], mix
(4) [100 g of solution (3) + 612 g water + 59.12 g sodium hydroxide], mix until dissolved
(5) [219.7 g sodium silicate solution + 612 g water + 59.12 g sodium hydroxide], mix until dissolved
(7) [(4) + (5)], combine quickly and stir for 30 minutes[d]

DropBooks

Crystallization

Vessel: polyethylene bottles
Temperature: 90°C [e]
Time: 8 hours
Agitation: none

Product Recovery

(1) Filter and wash to pH < 10
(2) Dry at 100°C, equilibrate over saturated aqueous NaCl
(3) Yield: near 100% on Al_2O_3

Product Characterization

XRD: 100% FAU, a_o = 24.92 Å, competing phases: LTA, GIS, ANA, SOD

Elemental Analysis: $NaAlO_2 \cdot 1.24\ SiO_2$[f]

Crystal Size and Habit: spherical aggregates, 0.8 μm dia.

References

[1] H. Lechert, H. Kacirek, Zeolites 11 (1991) 720
[2] H. Lechert, H. Kacirek, Zeolites 13 (1992) 192
[3] G. H. Kühl, Zeolites 7 (1987) 451

Notes

a. NaX zeolites are easily obtained with gel $SiO_2/NaAlO_2$ = 1.4-5.0, $NaOH/NaAlO_2$ = 3.8-20 and $H_2O/NaAlO_2$ = 150-400.

b. Crystallization at lower water contents suffers from the high initial viscosities of the batches, thus preventing sufficient homogenization. NaX can be obtained without precautions down to $H_2O/NaAlO_2$ = 80. The crystallizing zeolite and its composition depend strongly on the alkalinity being held in the solution phase during the nucleation and growth of the zeolite. For a given batch composition, if the water content is decreased appreciably, the alkalinity will increase. If there are reasons to decrease the water content, the NaOH content should be decreased. Good results were obtained by reducing the alkali content proportional to the water content.

c. For the batch preparation, the authors would always prefer sodium aluminate instead of alumina trihydrate. Problems often occurred with the solubility of the $Al(OH)_3$ at the given NaOH concentration, depending on the alumina source. Sodium aluminate is usually available only in technical-grade quality. If only small quantities of NaX or pure substances are desired, it was preferable to use $AlCl_3$ as the alumina source and to increase the NaOH content of the batch by 3 NaOH on the given batch composition to: $AlCl_3$: 4 SiO_2 : 20 NaOH : 325 H_2O. The resulting NaCl does not disturb the crystallization.

d. Longer times of homogenization give narrower particle size distributions.

e. Preferable crystallization temperatures: 67° to 97°C. For safety the crystallization time should be increased to 12 to 14 hours. Experiments have shown that in the given batches up to 30 hours at 90°C no other zeolite impurities were observed.

f. The Si/Al ratio of the product depends strictly on the NaOH concentration in the batch. Below 2.0 NaOH/liter, the nucleation rate of NaX goes almost to zero and nucleation of GIS occurs, which grows faster than NaX. Pure FAU with Si/Al > 1.5 in the product cannot be obtained without seeding. Above about 3.0 NaOH/liter, analcime or sodalite is obtained. Below Si/Al = 12.4, NaA appears. [3]

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Verified Syntheses of Zeolitic Materials. H. Robson, editor

FAU — Low-silica Type X (LSX) — Si(50.5), Al(49.5)

Contributed by Günter Kühl

Verified by M. Ludvig and by D. Millar

Type Material: $Na_{73}K_{22}Al_{95}Si_{97}O_{384} : wH_2O$

Method: G. H. Kühl [1]

Batch Composition: 5.5 Na_2O : 1.65 K_2O : Al_2O_3 : 2.2 SiO_2 : 122 H_2O[a-c]

Source Materials

distilled water
sodium aluminate (Nalco 680, 45.6% Al_2O_3, 29.65% Na_2O)
potassium hydroxide, reagent grade (usually ~86% KOH)
sodium hydroxide, reagent grade (usually ~97% NaOH)
sodium silicate solution (PQ Corp. N-brand clarified, 28.7% SiO_2, 8 .9% Na_2O)

Batch Preparation (for 29 g dry product)[d]

(1) [30 g water + 22.37 g sodium aluminate], stir until dissolved
(2) [70 g water + 21.53 g potassium hydroxide + 31.09 g sodium hydroxide], stir until dissolved
(3) [(1) + (2)], mix thoroughly [e]
(4) [(3) + 71.8 g water + 46.0 g sodium silicate solution], mix thoroughly [f]

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Crystallization

Vessel: sealed polypropylene or Teflon jar
Incubation: 3 hours at 70°C without stirring
Temperature: 93-100°C
Time: 2 hours
Agitation: either with or without stirring

Product Recovery

(1) Dilute the reaction mixture with distilled water
(2) Filter and wash with 0.01 N NaOH [g]
(3) Dry at ambient temperature (drying at 110-125°C acceptable)
(4) Yield: 99+% based on alumina

Product Characterization

XRD: FAU (a_o = 25.03 Å);[h] competing phases: LTA (when gel SiO_2/Al_2O_3 = 2.0), SOD (concentration is too high), P (extended aging or crystallization times)
Elemental Analysis: 0.77 $Na_2O \cdot 0.23\ K_2O \cdot Al_2O_3 \cdot 2.04\ SiO_2$
Crystal Size and Habit: multi-faceted spherulites of 2-6 μm dia. with 111 faces exposed [1]

Reference

[1] G. H. Kühl, Zeolites 7 (1987) 451

Notes

a. H_2O includes water from sodium aluminate, waterglass, free and bound water in NaOH + KOH, and added water.

b. $(K_2O + Na_2O)/SiO_2$ can be reduced to 2.25 without loss of product quality. However, at least for the initial crystallizations, a value of 3.25 is recommended.

c. The ratio: $Na_2O/(Na_2O + K_2O)$ is critical; it should be in the range 0.77 to 0.78.

d. Use plastic or stainless steel equipment throughout.

e. Solution (1) should be perfectly clear, but it is probably acceptable if a clear solution (3) is obtained after adding NaOH and KOH.

f. The mixture must not gel before it is well mixed. It usually takes several minutes before a gel if formed.

g. Wash or exchange in 0.01 N NaOH to prevent hydrolysis; low-silica X hydrolyzes as easily as NaA.

h. The lower SiO_2/Al_2O_3 ratio enhances the line intensities, the presence of K^+ attenuates them.

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FAU — Linde Type Y — Si(71), Al(29)

Contributed by David Ginter

Verified by G. Price and by C. Kuntz

Type Material: $Na_{56}[Al_{56}Si_{136}O_{384}] : 250\ H_2O$

Method; D. M. Ginter, A. T. Bell and C. J. Radke [1]

Batch composition[a]

Seed Gel (5% of Al): 10.67 $Na_2O : Al_2O_3 : 10\ SiO_2 : 180\ H_2O$

Feed Stock Gel (95% of Al): 4.30 $Na_2O : Al_2O_3 : 10\ SiO_2 : 180\ H_2O$

Overall Gel: 4.62 $Na_2O : Al_2O_3 : 10\ SiO_2 : 180\ H_2O$

Source Materials

deionized water

sodium aluminate solid (Strem Chemical,[b] 1.27 Na/Al, 6.1% H_2O)

sodium hydroxide pellets (J. T.Baker, 99% NaOH)

sodium silicate solution (PQ Corp, N Brand, 28.7 wt% SiO_2, 8.9 wt% Na_2O)[c]

Batch Preparation (for 32 g anhydrous product)

Seed Gel:

(1) [19.95 g water + 4.07 g sodium hydroxide + 2.09 g sodium aluminate], stir in 50 mL plastic bottle until dissolved

(2) [(1) + 22.72 g sodium silicate solution], stir moderately for at least 10 minutes; after stirring, cap the bottle and let the solution age at room temperature for 1 day[d]

Feedstock Gel:[e]

(3) [130.97 g water + 0.14 g sodium hydroxide + 13.09 g sodium aluminate], stir in a 500 mL plastic beaker until dissolved

(4) [(3) 142.43 g sodium silicate solution], stir vigorously with a high-shear turbine mixer[f] until the gel appears somewhat smooth; cover the beaker until the addition of the seed gel

Overall Gel:

(5) [(4) + 16.50 g of (2)], slowly add seed gel (2) to feedstock gel (4) under high shear;[f] move the beaker during mixing to ensure the entire gel volume encounters the high shear from the turbine (up to 20 minutes)[g]

Crystallization

Vessel: 300 mL polypropylene bottle (sealed)

Incubation: One day at room temperature [g]

Temperature: 100°C [g]

Time: After about 5 h, the gel will separate into a solid (containing the NaY Zeolite) that will settle to the bottom, and a hazy supernatant liquid. Continue heating until the supernatant is clear indicating complete crystallization (no more than 2 additional hours)[g]

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Product Recovery

(1) Centrifuge; decant supernatant
(2) Filter the wet solid product; wash with distilled water until pH of filtrate is below 9
(3) Dry at 110°C
(4) Yield: approximately 32 g of anhydrous NaY (about 98% on Al_2O_3)

Product Characterization

XRD: FAU; characteristic strong reflections at d = 14.28, 8.75 and 7.46 Å, a_o = 24.72 Å.

Competing phases (if present): GIS, GME, CHA
Elemental Analysis; $NaAlO_2 \cdot 2.43\ SiO_2$

Crystal Size and Habit: octahedral crystals, < 1 μm

References

[1] D. M. Ginter, A. T. Bell, C. J. Radke, in Synthesis of Microporous Materials, Vol. I, Molecular Sieves, M. L. Occelli, H. E. Robson (eds.), Van Nostrand Reinhold, New York, 1992, p 6
[2] T. Linder, C. Kurtz, personal communications

Notes

a. This procedure is reliable only for the production of submicron NaY crystals and is limited in the range of sizes and compositions that can be produced using slight procedural modifications.
b. Also available as solutions with this Na/Al ratio from Alcoa and U. S. Aluminate.
c. It should be clear of precipitated material.
d. Solution is clear when prepared; during aging, a loose gel forms which contains the NaY seeds.
e. May be prepared concurrently with the seed gel or just prior to mixing the overall gel.
f. 1600 rpm with 2.5 inch diameter, 4 paddle radial mixer (minimum) recommended.
g. If a GIS (NaP) impurity is produced, it can be eliminated by reducing the Na aluminate in (1) to 1.40 g and aging the seed gel for 1 to 5 days prior to blending it into the feedstock. Further aging of the composite is optional with this seed, and pure product has been obtained after crystallization at 90°C for 22 hours [2]

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FAU High-silica Faujasite EMC-1[a] Si(79), Al(21)

Contributed by Joël Patarin

Verified by C-n. Wu, by J. Dwyer, and by J. Zhao

Type Material: $Na_{40}[Al_{40}Si_{152}O_{384}] \cdot (15\text{-Crown-5})_8 : (H_2O)_{60}$

Method: T. Chatelain, J. Patarin, M. Soulard, J.-L. Guth, P. Schulz [1]

Batch Composition: 2.1 Na_2O : 10 SiO_2 : Al_2O_3 : 0.5(15-crown-5) : 100 H_2O

Source Materials

distilled water
crown ether (Aldrich 15-crown-5, 98%)
sodium hydroxide (Fluka, 98%)
sodium aluminate (Carlo Erba, 56% Al_2O_3, 37% Na_2O)
silica sol (Ceca, 40% SiO_2)

Batch Preparation[b] (for 15 g product)[c]

(1) [17.75 g water + 2.25 g crown ether], dissolve under continuous stirring
(2) [(1 + 1.65 g sodium hydroxide], dissolve under continuous stirring
(3) [(2) + 3.64 g sodium aluminate], dissolve under continuous stirring
(4) [(3) 30.00 g silica sol] stir with a magnetic bar at approximately 200 rpm Continue stirring for 24 hours at room temperature.[d] Gel pH = 13.5-14

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Crystallization

Vessel: Teflon-lined stainless steel autoclave (150 mL)
Temperature: 110°C
Time: 8 days
Agitation: none
Final pH = approximately 12.5

Product Recovery

(1) Filter and wash with distilled water until pH of the filtrate is close to 6
(2) Dry at 60-70°C overnight
(3) Yield: 99% based on alumina (as-synthesized product containing the organic template and some water)[e]

Product Characterization

XRD: FAU, a_o = 24.57 Å

Elemental Analysis: SiO_2/Al_2O_3 7.6 (by atomic absorption spectroscopy and ^{29}Si MAS NMR)

Crystal Size and Habit: truncated octahedra, 1 μm dia.

References

[1] T. Chatelain, J. Patarin, M. Soulard, J.-L. Guth, P. Schulz, Zeolites 15 (1995) 90
[2] D. Anglerot, F. Fitoussi, P. Schulz, T. Chatelain, F. Dougnier, J. Patarin, J.-L. Guth, in Synthesis of Porous Materials, Zeolites, Clays and Nanostructures, M. L. Occelli, H. Kessler (eds.), Marcel Dekker, New York, 1996, p. 325

Notes

a. EMC-1 = Elf Mulhouse Chemistry number one.
b. The starting mixture is prepared in a polypropylene bottle.
c. This synthesis has been successfully carried out at the kilogram scale [2].
d. The mixture is aged in a closed polypropylene bottle.
e. Calcination at 450°C in air removes the template.

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FAU [Ga] Type Y Si (61), Ga (39)

Contributed by Mario Occelli

Verified by F. Machado, by S. Iwamoto, and by M. Levinbuk

Type Material: $Na_{76}Ga_{76}Si_{116}O_{384} : wH_2O$

Method: M. L. Occelli [1]

Batch Composition: 4.0 Na_2O : Ga_2O_3 : 9.8 SiO_2 : 150 H_2O

Source Materials

deionized water
sodium hydroxide, reagent grade (usually ~97% NaOH)
gallium oxide (99.99%)
silica sol (Dupont HS-40, 39% SiO_2, 0.5% Na_2O)

Batch Preparation

(1) [32.0 g water + 32.0 g sodium hydroxide + 18.7 g gallium oxide], dissolve gallium oxide in 50% NaOH at 80°C with stirring until a clear solution is obtained. Cool to ambient temperature
(2) [(1) + 70.6 g water], mix [a]
(3) [150.2 g silica sol + 70 g water], mix
(4) [(3) + (2)], add the sodium gallate solution dropwise to the vigorously-stirred, diluted silica sol. Continue stirring for 16 hours at ambient temperature

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Crystallization

Vessel: one-liter round-bottomed flask with reflux condenser
Incubation: 16 h at 25°C with stirring
Temperature: 95°C[b]
Time: 90 hours[c]

Product Recovery

(1) Filter and wash with deionized water until pH < 10
(2) Dry at 110°C
(3) Yield: near 100% on Ga_2O_3

Product Characterization

XRD: FAU; no other crystalline phases or amorphous material observed
Elemental Analyses: 38.7 wt% Ga_2O_3, 38.0 wt% SiO_2, 12.5 wt% Na_2O (0.98 $Na_2O \cdot Ga_2O_3 \cdot 3.06\ SiO_2$)[d]

References

[1] M. L. Occelli, US Patent 4 803 060 (1989)
[2] M. L. Occelli, A. E. Schweizer, H. Eckert, A. Auroux, P. S. Iyer, Appl. Catalysis (to be submitted)

Notes

a. Diluted sodium gallate solution must be clear.
b. The temperature of the stirred, cold-aged hydrogel is raised to 95°C. When the hydrogel reaches 95°C the stirring is immediately stopped.
c. Method to reduce crystallization time given in ref. [1, 2]
d. After calcination at 600°C for 2 h; BET surface area 541 m^2/g.

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FAU SAPO-37 Al(47), P(36) Si(17)

Contributed by M. J. Franco and J. Pérez-Pariente

Verified by J. Patarin and by M. Ribeiro

Type Material: (7TMA, 13TPA)[$Al_{90}Si_{33}P_{69}O_{384}$]
(TMA = tetramethyl ammonium, TPA = tetra-n-propyl ammonium)

Method: M. J. Franco, J. Pérez-Pariente, A. Mifsud, T. Blasco, J. Sanz [1]

Batch Composition: $0.025(TMA)_2O : 1.0(TPA)_2O : 1.0Al_2O_3 : 1.0P_2O_5 : 1.0SiO_2 : 50H_2O$

Source Materials
deionized water
phosphoric acid (Riedel-de Häen, 85% H_3PO_4)
alumina (pseudoboehmite, Vista, 70% Al_2O_3)[a]
tetrapropylammonium hydroxide (TPAOH), Alfa, 40% aqueous solution)[b]
tetramethylammonium hydroxide ($TMAOH \cdot 5H_2O$, Aldrich, 99%)
fumed silica (Aerosil 200, Degussa)

Batch Preparation (for 6.2 g product)[c]
(1) [20.69 g water + 23.04 g phosphoric acid + 14.56 g alumina]. Mix water and phosphoric acid at 293K and add the alumina very slowly with vigorous stirring (1500 rpm). Continue stirring for 8 hours at 293K in a temperature-controlled bath
(2) [101.68 g tetrapropylammonium hydroxide (40% solution) + 0.90 g tetra-methylammonium hydroxide + 6.00 g silica]. Dissolve the TMAOH in the TPAOH solution in a separate glass beaker. To this solution add the silica under vigorous stirring. Continue stirring for one hour
(3) [(1) + (2)] Add silicate solution (2) slowly to aluminate slurry (1) under vigorous stirring. Continue stirring for 24 hours at 293K. The final gel pH should be approximately 7.5

Crystallization
Vessel(s): 60 mL Teflon-lined stainless steel autoclave(s)
Temperature: 200°C [d]
Time: 13 hours
Agitation: none

Product Recovery
(1) Quench autoclave in cold water
(2) Recover solids by centrifugation (6000 rpm)
(2) Wash with cold distilled water
(4) Dry at 80°C for 16 hours
(5) Yield: 3.7 g solid/100 g of gel (19% on Al_2O_3)

Product Characterization

XRD: FAU-type, pure. Competing phases: AFI and SOD when other compositions and/or crystallization treatments are used

Elemental Analysis: $(Si_{0.17}Al_{0.47}P_{0.36})_{192}O_{384} \cdot 3.5(TMA)_2O \cdot 6.5(TPA)_2O$[e]

Crystal Size and Habit: Crystals are quite homogeneous in size (approximately 4.0 μm dia.) and show interpenetrating octahedra morphology [f]

Reference

[1] M. J. Franco, J. Pérez-Pariente, A. Mifsud, T. Blasco, J. Sanz, Zeolites 12 (1992) 386

Notes

a. B.E.T. surface area 271 m2/g; the alumina may be critical. Aluminum isopropoxide gave negative results.

b. Commercial 20% TPAOH can be vacuum stripped to 40%; however it is critical to make sure that there has not been decomposition of the TPAOH. For this reason, it is necessary to make a OH^- titration before and after the evaporation process to check that the total amount of OH^- has not changed. (Na + K) < 340 ppm

c. During preparation of the gel, it is very important to use a closed vessel and a temperature controlled bath (293K) to ensure a constant water concentration in the gel. This vessel can be a polypropylene bottle with a hole in the cap to fit the rotating shaft of the stirring device. A stirring device with two movable Teflon blades is recommended.

d. Heat-up rate: 2.5°/min.; autogenous pressure.

e. Flow thermogravimetric analysis showed three different weight losses: 373 to 473K (water desorption), 473 to 688K (decomposition of TPA^+ in the alpha cages),588 to 973K (decomposition of TMA^+ in the sodalite cages).

f. Increasing $(TPA)_2O/Al_2O_3$ in gel from 1.0 to 1.5 (keeping $TPA^+/TMA^+ = 40$) decreased average crystal diameter from 4 to 2 μm and increased product yield by 100%. [1]

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FER ZSM-35 Si(87), Al(13)

Contributed by Jinxiang Dong

Verified by S. Weigel, by L. Schreyeck, and by T. Beelen

Type Material: $Na_5[Al_5Si_{31}O_{72}] : wH_2O$ (w ~ 18)

Method: P. A. Jacobs, J. A. Martens [1]

Batch Composition: 1.85 Na_2O : Al_2O_3 : 15.2 SiO_2 : 592 H_2O : 19.7 C_2DN [a] (C_2DN = ethylenediamine)

Source Materials
distilled water
sodium hydroxide (Merck, reagent grade)
sodium aluminate (Hopkin & Williams, technical grade)[b]
silica sol (Dupont Ludox AS-30, 30% SiO_2)
ethylenediamine (Merck, reagent grade)

Batch Preparation (for 10 g dry product)
(1) [129 g water + 0.7 g sodium hydroxide + 3.3 g sodium aluminate], stir until dissolved
(2) [46.47 g silica sol + 18.3 g C_2DN], mix
(3) [(1) + (2)], mix thoroughly

Crystallization
Vessel: stainless steel autoclaves (250 mL)
Temperature: 177°C
Time: 10 days
Agitation: 15 rpm, tumbling [2]

Product Recovery
(1) Filter solid products and wash with distilled water
(2) Dry at 120°C
(3) Yield: 60% on SiO_2

Product Characterization
XRD: FER (only crystalline phase); Competing phases: quartz, MOR, MFI
Elemental Analysis: SiO_2/Al_2O_3 = 13
Crystal Size and Habit: irregular, approximately 1 μm long

References
[1] P. A. Jacobs, J. A. Martens, Stud. Surf. Sci. Catal. 33 (1987) 217
[2] L. Schreyeck, personal communication
[3] C. L. Kibby, A. J. Perrota, F. E. Massoth, J. Catal. 35 (1974) 256
[4] W. Xu, J. Li , W. Li, H. Zhang, B. Liang, Zeolites 9 (1989) 468

Notes
a. Hydrothermal syntheses using different organic additives are reported in the literature, particularly pyrrolidine [1] and tetramethyl-ammonium cation [3]. Nonaqueous methods based on ethylenediamine plus triethyl-amine give good crystallinity and improved yield.[4]
b. Assumed 1.28 Na/Al, 16% H_2O

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GIS — Zeolite P — Si(54), Al(46)

Contributed by Lovat V. C. Rees

Verified by Yingcai Long, by P. Sidheswaran, and by G. Price

Type Material: $(NaAlO_2)_7(SiO_2)_9$

Method: L. V. C. Rees and S. Chandrasekhar [1]

Batch Composition: $Al_2O_3 : 2.2\ SiO_2 : 5.28\ NaF : 105.6\ H_2O$

Source Materials
distilled water
sodium fluoride (BDH Analor)
kaolinite ($Al_2O_3 : 2.2\ SiO_2 : 2\ H_2O$)[a]

Batch Preparation (for 10 g dry product)
(1) [87.7 g water + 10.4 g sodium fluoride], stir and make a slurry
(2) [(1) + 12.7 g kaolin], mix thoroughly

Crystallization
Vessel: sealed polypropylene
Time: 60 days
Temperature: 85°C
Agitation: none
pH: initial 7.5, final 9-10

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Product Recovery
(1) Filter and wash thoroughly with distilled water
(2) Exchange twice with NaCl solution
(3) Wash with distilled water (adjusted to pH = 10 with NaOH)
(4) Dry at 85°C for 24 hours
(5) Rehydrate over water vapor from saturated NaCl solution

Product Characterization
XRD: Strong zeolite P; competing phases: CHA, no SOD
Elemental Analysis: $NaAlO_2 \cdot 1.18\ SiO_2$ (by atomic absorption spectroscopy)[b,c]
Crystal Size and Habit: spherulitic particles of approximately 10 μm dia.

Reference

[1] L. V. C. Rees, S. Chandrasekhar, Zeolites 13 (1993) 535

Notes

a. Kaolinite from Trivandrum, Kerela, India
b. Dissolution of the zeolite sample for atomic adsorption: 0.1 g sample was treated with 30 mL of a mixture of HCl (37%), HF (48%) and distilled water (ratio 1:1:1); the same was kept for two to three days for complete dissolution.
c. ^{29}Si MAS NMR gave five lines with chemical shifts of -86.79, -91.55, -97.19, -102.86 and -107.10 ppm. ^{27}Al MAS NMR gave two lines, intense Al (tet) at 58.58 and weak (oct) at -0.42 ppm.

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KFI ZK-5 Si(77), Al(23)

Contributed by J. P. Verduijn

Verified by J. Patarin, by J. Kornatowski, and by S. Ahmed

Type Material: $K_{22}[Al_{22}Si_{74}O_{192}] : w\ H_2O$

Method: J. P. Verduijn [1]

Batch Composition: $2.30\ K_2O : 0.1\ Sr(NO_3)_2 : Al_2O_3 : 10\ SiO_2 : 160\ H_2O$

Source Materials

deionized water
potassium hydroxide (Baker 0222, pellets, 86.8% KOH)
alumina (Baker 0005, 98.6% $Al(OH)_3$)
silicic acid (AKZO SM 604, 90% SiO_2)[a]
strontium nitrate (Fluka 85900)[b]

Batch Preparation (for 57 g product)

(1) [50.00 g water + 29.76 g potassium hydroxide + 15.80 g alumina], heat to boiling until clear; cool to room temperature and correct weight loss due to boiling
(2) [96.97 g water + 66.77 g silicic acid], mix until smooth (approximately 6 minutes)
(3) [75.08 g water + 2.124 g strontium nitrate], mix until dissolved
(4) [(2) + (3) + 25.12 g water (rinse)], mix for 6 minutes
(5) [(4) + (1) + 25.08 g water (rinse)], mix for 6 minutes [c]

Crystallization

Vessel: 300 mL stainless steel autoclave[d]
Time: 115 hours[e]
Temperature: 150°C[f]
Agitation: none

Product Recovery

(1) Cool to room temperature [g]
(2) Filter and wash (5 times) with 650 mL water; the pH of the last wash water = 10.5
(3) Dry in a 150°C oven for 16 hours
(4) Yield: 57.2 g (97% on Al_2O_3)

Product Characterization

XRD: KFI (only crystalline product)
Elemental Analysis: $SiO_2/Al_2O_3 = 6.6$
Crystal Size and Habit: ~ 0.5 μm

Reference

[1] J. P. Verduijn, US Patent 4 944 249 (19 February 1991)

Notes

a. Colloidal silicas such as Ludox HS-40 are also suitable silica sources.
b. The Sr^{2+} sources used were $Sr(OH)_2$ and $Sr(NO_3)_2$; there is no preference.
c. The final gel is (visually) very homogeneous and pourable.
d. No Teflon liner was used.
e. Crystallization times (at 150°C) are not critical (90-140 hours).
f. The autoclave was placed in a room temperature oven. The oven was heated within 2 hours to 150°C and kept at this temperature for 115 hours.
g. The synthesis magma (after treatment has an amorphous appearance; no free mother liquor can be seen. This is typical for this type of synthesis.

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KFI — High-silica KFI — Si(79), Al(21)

Contributed by Alain Matijasic and Joël Patarin

Verified by S. Schwarz, by K. Strohmaier, and by S. Miller

Type Material: $K_{18}Sr[Al_{20}Si_{76}O_{192}] \cdot 72\ H_2O \cdot$ (18-C-6) (18-C-6 = Cycl. $(C_2H_4O)_6$)

Method: T. Chatelain, J. Patarin, R. Farré, O. Pétigny, P. Schulz [1]

Batch Composition: 2.3 K_2O : 0.1 SrO : Al_2O_3 : 10 SiO_2 : 220 H_2O : 1.0(18-C-6)

Source Materials

distilled water
potassium hydroxide (Prolabo, 86% KOH)
aluminum hydroxide (Fluka, 99+% $Al(OH)_3$)
strontium nitrate (Prolabo >97% $Sr(NO_3)_2$)
silica sol (Dupont Ludox AS-40, 40% SiO_2)
18-C-6 (Lancaster, > 98% cycl. $(C_2H_4O)_6$)

Batch Preparation (for 7 g of as-synthesized product)

(1) [11.00 g water + 3.00 g potassium hydroxide + 1.57 g aluminum hydroxide], heat to boiling until clear, cool to room temperature and correct weight loss due to boiling [a]
(2) [18.63 g water + 0.22 g strontium nitrate + 2.70 g 18-C-6 + 15.00 g silica sol], stir until homogenized
(3) [(1) + (2)], mix for 30 min. (forms a thick gel). Transfer to a 120 mL PTFE-lined stainless steel autoclave. Final pH: 14

Crystallization

Vessel: PTFE-lined stainless steel autoclave
Time: 120 hours
Temperature: 150°C in a preheated oven
Agitation: none; final pH: approximately 13

Product Recovery

(1) Dilute the reaction mixture with distilled water
(2) Filter and wash until pH ≈ 10
(3) Dry at 60°C overnight
(4) Yield: Total ≈ 7 g of as-synthesized KFI-type sample (product contains 18-C-6 as organic template, ~ one molecule per unit cell [b]

Product Characterization

XRD: Highly crystalline KFI; can be indexed with cubic symmetry, a_o=18.671(1)Å[b]

Elemental Analyses: Si/Al = 3.7[b]

Crystal Size and Habit: by SEM, the crystals display a cubic morphology; most of them are aggregated and their sizes range from 2 to 4 μm

Reference

[1] T. Chatelain, J. Patarin, R. Farré, O. Pétigny, P. Schulz, Zeolites 17 (1996) 328

Notes

a. The starting mixture is prepared in a polyethylene vessel.
b. According to ref. [1].

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LEV [B]-Levyne Si(89), B(11)

Contributed by Giuseppe Bellussi and Angela Carati

Verified by Li Shi and by S. B. Hong

Type Material: $(Na,H)_5[B_5Si_{49}O_{108}] : 8\ Q : 5\ H_2O$[a] (Q = quinuclidine)

Method: R. Millini, A. Carati, G. Bellussi [1]

Batch Composition: $3.0\ Q : B_2O_3 : 3.0\ SiO_2\ 60\ H_2O$

Source Materials
distilled water
quinuclidine (1-azabicyclo[2.2.2]octane) (Aldrich, 97%)
boric acid (H_3BO_3) (Carlo Erba RPE-ACS)
silica sol (Dupont HS-40, 40% SiO_2, 0.3% Na_2O)

Batch Preparation (for 19 g dry product)
(1) [10 g water + 14.7 g quinuclidine], mix until dissolved
(2) [61 g water + 10.8 g boric acid + 14.7 g quinuclidine], mix until dissolved
(3) [39.5 g silica sol + (1)], mix until a uniform gel is obtained
(4) [(3) + (2)], add solution (2) to gel slowly with vigorous mixing. Final slurry pH ~ 11

Crystallization
Vessel: stainless-steel autoclave
Time: 5 days
Temperature: 170°C
Agitation: autoclave is rotated 20 rpm

Product Recovery
(1) Filter to recover solids
(2) Wash with distilled water
(3) Dry at 120°C
(4) Yield: 90% on SiO_2

Product Characterization
XRD: LEV (only crystalline phase), a = 12.944 Å, c = 21.914 Å
Elemental Analysis: $17\ SiO_2 : B_2O_3 : 2.7\ Q$ (dry basis)[b]
Crystal Size and Habit: Compact spherical aggregates (4 to 8 μm) of small crystals

Reference
[1] R. Millini, A. Carati, G. Bellussi, Zeolites 12 (1992) 265

Notes
a. Protonated quinuclidine (HQ^+) or Na^+ (from silica sol) act as counterions for structural boron.
b. By thermal analysis, organic material adsorbed in extra framework pores is eliminated at 268°C. After treatment at 550°C for a few hours, a limited structure collapse is observed with formation of amorphous material and trigonal BO_3 units. [1]

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Verified Syntheses of Zeolitic Materials. H. Robson, editor

LTA — Linde Type A — Si(50), Al(50)

Contributed by R. W. Thompson and K. C. Franklin

Verified by B. Subotic and A. Cizmek, and by K. Hashimoto

Type Material: $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] : 27\ H_2O$

Method: R. W.Thompson, M. J. Huber [1]

Batch Composition: $3.165\ Na_2O : Al_2O_3 : 1.926\ SiO_2 : 128\ H_2O$[a]

Source Materials

deionized water
sodium hydroxide (Fisher Scientific, 99+% NaOH)
sodium aluminate (Fisher Scientific, $NaO_2 : Al_2O_3 : 3\ H_2O$)[b]
sodium metasilicate (Fisher Scientific, $Na_2SiO_3 : 5\ H_2O$)

Batch Preparation (for 10 g dry product)

(1) [80 mL water + 0.723 g sodium hydroxide], mix gently until NaOH is completely dissolved. Divide into two equal volumes in polypropylene bottles
(2) [One-half of (1) + 8.258 g sodium aluminate], mix gently in capped bottle until clear [c]
(3) [Second half of (1) + 15.48 g sodium metasilicate], mix gently in capped bottle until clear [c]
(4) [(2) + (3)], pour silicate solution into aluminate solution quickly; a thick gel should form. Cap tightly and mix until homogenized [d]

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Crystallization

Vessel: 100-150 mL polypropylene bottle (sealed)
Incubation: none required
Temperature: 99 ± 1°C
Time: 3-4 hours[e]
Agitation: stirred or unstirred

Product Recovery

(1) Remove from heat source and cool to below 30°C
(2) Filter to recover solids and wash with deionized water until filtrate pH is below 9 [f]
(3) Dry product on filter paper and watch glass at 80-110°C overnight
(4) Yield: 28.1 g (hydrated) or 10.4 g (dry)

Product Characterization

XRD: LTA; characteristic strong reflections at d = 4.107, 3.714, 3.293 and 2.987 Å Competing phases (if present): SOD (HS), GIS (Pc)
Elemental Analysis: $Na_2O \cdot Al_2O_3 \cdot 2\ SiO_2$
Crystal Size and Habit: cubic crystals, 2-3 μm[g]

References

[1] R. W. Thompson, M. J. Huber, J. Cryst. Gr. 56 (1982) 711
[2] D. W. Breck, Zeolite Molecular Sieves, John Wiley, New York, 1974, p 270
[3] J. F. Charnell, J. Cryst. Gr. 3 (1971) 291
[4] H. Neels, W. Schmitz, E.-M. Berger, D. Lutz, Krist. Tech. 13 (1978) 1345
[5] G. Scott, A. G. Dixon, A. Sacco, Jr., R. W. Thompson, in Stud. Surf. Sci. Catal. 49, P. A. Jacobs, R. A. Van Santen (eds.), Elsevier, Amsterdam,1989, p 363

Notes

a. Zeolite NaA can be synthesized from a wide range of batch compositions as noted in Breck [2] and temperatures other than used in this example, *e.g.*, 60-110°C. Also, it can be made from a variety of alumina and silica source materials other than those used in this example, *e.g.*, pure aluminum powder[h] or aluminum wire, fumed silica, sodium disilicate, Ludox, silica gels, etc. The actual weights of these other sources used must be compensated for the presence of water of hydration, Na^+ ions, etc.

b. Assumed 100%.

c. Could take 10-20 minutes.

d. May be done with laboratory mixer or vigorously by hand for 5-10 minutes.

e. The turbid gel phase will be observed to diminish in height as the reaction proceeds, accelerating rapidly in the final stages of the crystallization, leaving a clear supernatant above the precipitated crystalline phase.

f. One-half liter should be sufficient for this preparation.

g. Zeolite NaA crystals are typically cubic. Dodecahedral crystals have been observed frequently, but there is little fundamental understanding of why this habit forms. Additions of triethanolamine are known to result in larger crystals, but the particle size distribution becomes broader, synthesis times are extended, and the impurity zeolite phases appear with increased abundance. [3-5]

h. Special care must be taken if powdered aluminum is dissolved in a caustic solution to make the aluminate solution. Since its dissolution is exothermic, the solution can become quite warm and hydrogen evolves.

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Verified Syntheses of Zeolitic Materials. H. Robson, editor

LTA ZK-4 Si(59), Al(41)

Contributed by Don Hopkins

Verified by V. Valtchev, by M. Castagnola, and by G. Kühl

Type Material: $Na_{9.2}(TMA)_{0.8}[Al_{10}Si_{14}O_{48}]$ (TMA = tetramethylammonium)

Method: G. T. Kerr [1]

Batch Composition: 1.55 Na_2O : Al_2O_3 : 3.91 SiO_2 : 4.13$(TMA)_2O$: 320 H_2O

Source Materials

distilled water
sodium hydroxide (50% solution)
sodium aluminate (~46% Al_2O_3, 31% Na_2O; Fisher, MC&B, Nalco)
tetramethylammonium hydroxide (TMA-OH, Southwestern Analytical Chemical, 25% aqueous solution)
silica sol (Dupont HS-40 or AS-40, 40% SiO_2)

Batch Preparation (for 34 g product)

(1) [290 g water + 6.0 g sodium hydroxide solution + 21.5 g sodium aluminate], stir until dissolved
(2) [292 g TMA-OH (25% solution) + 57.0 g silica sol], stir for approximately 30 minutes
(3) [(1) + (2)], stir vigorously; gel pH = 14.0 to 14.5

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Crystallization

Vessel: Teflon bottle, 1000 mL
Incubation: 24 hours at 25°C (optional)
Temperature: 100°C (oven with efficient air circulation)
Time: 16-48 hours
Agitation: none

Product Recovery [a]

(1) Filter and wash with 0.5 to 1 L water
(2) Dry at 100°C
(3) Yield: approximately 34 g (100% on Al_2O_3)

Product Characterization

XRD: LTA, a_o = 24.38 Å; competing phases: GIS (long reaction time) and EAB [b]

Elemental Analysis (dried at 100°C): 15.7% Al (29.7% Al_2O_3), 23.1% Si (49.4% SiO_2), 12.4% Na (16.7% Na_2O), 2.24% C (3.83% $(TMA)_2O$)[c]

Crystal Size and Habit: cubes (some with penetration twinning) approximately 1.0-1.5 μm on an edge

References

[1] G. T. Kerr, Inorg. Chem. 5 (1966) 1537
[2] R. H. Jarman, M. T. Melchior, D. E. W. Vaughan, ACS Symposium Series 218, American Chemical Soc., Washington, D. C., 1983, p 267

Notes

a. Although no decomposition of TMA-OH is expected, it is advisable to carry out the crystallization and product work-up in a fume hood. Temperature excursions can produce noxious and toxic by-products, *e.g.*, trimethylamine and methanol.
b. EAB can co-precipitate with ZK-4 if the TMA-OH is added to solution (1) before the silica sol.
c. The Si/Al of products by this recipe ranged from 1.39 to 1.43 (average 1.41). Higher and lower Si/Al products have been made using other recipes. [2]

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LTA Zeolite Alpha Si(75), Al(25)

Contributed by Günter Kühl

Verified by S. Mintova and by Zhaolan

Type Material: $Na_4(TMA)_2[Al_6Si_{18}O_{48}]$ (TMA = tetramethylammonium)

Method: G. H. Kühl [1]

Batch Composition: 1.07 Na_2O : 2.37 $(TMA)_2O$: Al_2O_3 : 10 SiO_2 : 120 H_2O

Source Materials

distilled water
sodium aluminate (MCB, 28.5% Na_2O, 42.75% Al_2O_3)
tetramethylammonium hydroxide solution (25% TMAOH)[a]
precipitated silica (PPG Corp. Hi-Sil 233, 88% SiO_2)[b]

Batch Preparation (for 36 g product)

(1) [46.4 g water + 15.6 g sodium aluminate], stir at room temperature until dissolved[c]
(2) [(1) + 111.7 g tetramethylammonium hydroxide solution], mix
(3) [(2) + 44.5 g precipitated silica], add silica to the aluminate solution gradually with stirring[d]
(4) Stir or blend for 30 minutes[d]

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Crystallization

Vessel: polypropylene bottle
Incubation: 48 h at room temperature
Time: 24 - 30 hours[e]
Temperature: 90°C
Agitation: none

Product Recovery

(1) Dilute reaction mixture with water
(2) Filter on a dense filter, such as Whatman #5, or separate by decantation, then reslurry sediment, flocculate,[f] and and wash with water [g]
(3) Dry at room temperature or at 110°C
(4) Yield: 36 g (near 100% on Al_2O_3)

Product Characterization

XRD: LTA (contracted unit cell); competing phase: high-silica sodalite
Elemental Analyses: 0.6 Na_2O : 0.4 $(TMA)_2O$: Al_2O_3 : 6 SiO_2
Crystal size and habit: cubes, < 1 μm on edge

Reference

[1] G. H. Kühl, US Patent 4 191 663

Notes

a. TMA salts cannot be used because the anions tend to cause nucleation of high-silica sodalite ($SiO_2/Al_2O_3 = 10$).

b. Hi-Sil 233 has a median particle size of 18-19 μm; precipitated silica of larger particle size tends to be insufficiently reactive. Ultrasil 320 is an acceptable substitute. If less reactive silica is to be used in this preparation, 10% of the silica should be slurried in the (TMA)OH solution prior to combining the (TMA)OH with the $NaAlO_2$ solution.

c. Small amounts of iron may be removed by filtration although this iron does not affect the crystallization. If the sodium aluminate does not dissolve completely, it probably contains $Al(OH)_3$ and cannot be used.

d. Slow addition of Hi-Sil is recommended for proper dispersion. Silica-rich gel particles tend to cause nucleation of high-silica sodalite.

e. The longer crystallization time improves the crystallinity, unless sodalite nuclei are present.

f. Avoid flocculating in the presence of mother liquor because colloidal silica will coagulate.

g. Alternatively, use repeated decantation and reslurrying sequences (settling may be accelerated by centrifuging), and optionally, flocculation[h] after having removed the bulk of the alkalinity.

h. See Introductory Article on "Product Recovery."

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LTA $GaPO_4$ P(50), Ga(50)

Contributed by Henri Kessler and Abdallah Merrouche

Verified by P. Behrens, by P. Feng, by J. Chen, by R. Fricke, and by G. Férey

Type Material: $[Ga_{12}P_{12}O_{48}][(n\text{-}C_3H_7)_2NH_2F]_3 : (H_2O)w$ (w ~ 6 [1])

Method: A. Merrouche, J. Patarin, M. Soulare, H. Kessler, P. Anglerot [2]

Batch Composition: 1 Ga_2O_3 : 1 P_2O_5 : 1 HF : 70 H_2O : 6.5 DPA (DPA = di-n-propylamine)

Source Materials

phosphoric acid (Fluka, 85% H_3PO_4)
distilled water
gallium sulfate hydrate (Strem Chemicals, $Ga_2(SO_4)_3 \cdot xH_2O$ (wt% Ga ~ 18))
hydrofluoric acid (Fluka, 40% HF)
di-n-propylamine (Fluka, 95%)

Batch Preparation (for 1 g dry product)

(1) [1.16 g phosphoric acid + 2.2 g water + 3.8 g gallium sulfate hydrate + 2.5 g water], stir until dissolved
(2) [(1) + 0.25 g hydrofluoric acid], mix thoroughly
(3) [(2) + 3.25 g di-n-propylamine], mix thoroughly. Initial pH = 4 to 4.5

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Crystallization

Vessel: PTFE-lined autoclave
Temperature: 140°C
Time: 24 hours
Agitation: none

Product Recovery

(1) Filter; wash with distilled water
(2) Dry at 60°C
(3) Yield: approximately 60% with respect to starting oxides

Product Characterization

XRD: characteristic strong reflections at d = 12.02, 8.50, 6.94, 6.01 Å
Elemental Analysis (anhydrous form): $Ga_{0.49}P_{0.51}O_2(DPA)_{0.13}F_{0.12}$
Crystal Size and Habit: cubes (5 - 40 μm)

References

[1] A. Simmen, J. Patarin, C. Baerlocher, in Proceedings of the 9th International Zeolite Conference, Vol. I, R. Von Ballmoos, J. B. Higgins, M. M. J. Treacy (eds.), Montreal, 1992, Butterworth-Heinemann, Stoneham, 1993, p. 433
[2] A. Merrouche, J. Patarin, M. Soulard, H. Kessler, D.Anglerot, in Molecular Sieves, Vol. 1, Synthesis of Microporous Materials, M. L. Occelli, H. E. Robson (eds.), Van Nostrand Reinhold, New York, 1992, p. 384

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LTL Linde Type L Si(76), Al(24)

Contributed by J. P. Verduijn

Verified by C. Williams, by M. Uguina, and by J. Warzywoda

Type Material: $K_9[Al_9Si_{27}O_{72}] : wH_2O$ (w = 0 to 36)

Method; J. P. Verduijn [1]

Batch Composition: 2.35 K_2O : Al_2O_3 : 10 SiO_2 : 160 H_2O : trace MgO [a]

Source Materials

deionized water
potassium hydroxide (Baker 0222 pellets, 86.8% KOH)
alumina (Baker 0005, 92.6% $Al(OH)_3$)
silica sol (Dupont Ludox HS-40, 40% SiO_2)
magnesium nitrate (Baker, $Mg(NO_3)_2 \cdot 6\ H_2O$)

Batch Preparation (for ~ 59 g product)

(1) [50.00 g water + 30.39 g potassium hydroxide + 15.82 g alumina], heat to boiling until clear. Cool to room temperature and correct water loss due to boiling
(2) [150.24 g silica sol + 99.0 g water + 14.5 g $Mg(NO_3)_2$ solution],[b] mix until homogeneous (~ 3 minutes)
(3) [(1) + (2) + 25.00 g water (rinse)],[c] mix until thickening starts (~ 3 minutes) [d]

Crystallization

Vessel: 300 mL stainless steel autoclave[e]
Temperature: 175°C
Time: 48 hours[f]
Agitation: none

Product Recovery

(1) Cool to room temperature
(2) Filter and wash (5 times) with 650 mL water. The pH of the last wash water should be ~ 10
(3) Dry at 150°C for 16 hours
(4) Yield: After drying at 150°C, ~ 15.3 wt% based on the weight of synthesis gel in the autoclave (nearly 100% on Al_2O_3)

Product Characterization

XRD: LTL (only crystalline product). Competing phases: MER (without MgO)
Elemental Analysis: 6.2 SiO_2/Al_2O_3, 1.0 K_2O/Al_2O_3
Crystal Size and Habit: cylindrical, 0.2 to 0.4 μm diameter, 0.4 to 0.7 μm long (L/D ~ 2)

Reference

[1] J. P. Verduijn, US Patent 5 242 675 (1993)

Notes

a. The synthesis mixture contains 9 wt ppm of added Mg^{2+} species (based on the weight of the synthesis mixture).

b. $Mg(NO_3)_2$ solution: dissolve 2.5645 g magnesium nitrate ($Mg(NO_3)_2 \cdot 6\ H_2O$) in 997.4 g water.

This solution contains 0.24 mg Mg^{2+}/g solution. The function of the Mg^{2+} species is to avoid the formation of byproducts such as MER, and to control the particle size of the LTL product.

c. This water is used to quantitatively transfer the aluminate solution.

d. After 3 minutes mixing, the gel is still pourable. Longer mixing is permitted, but the gel then tends to stiffen and is difficult to transfer to the autoclave.

e. No Teflon liner was used.

f. Crystallization time is not critical (24 to 72 hours).

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MAZ Mazzite Si(78), Al(22)

Contributed by David Vaughan and Karl Strohmaier

Verified by S. Yang and A. Navrotsky, by C. Williams and C. Round, by Hyun-ku Rhee, and by J. Kornatowski

Type Material: $Na_{7.3}(TMA^+)_{0.7}Al_8Si_{28}O_{72} : wH_2O$ (TMA = tetramethylammonium)

Method: D. E. W. Vaughan [1]

Batch Composition: 3.35 Na_2O : 1.24 (TMA)Br : Al_2O_3 : 9.17 SiO_2 : 125 H_2O : 0.66 Na_2SO_4

Source Materials

deionized water
sodium hydroxide (J. T. Baker, ~ 99% NaOH)
alumina (Alcoa C-31, assumed 100% $Al_2O_3 \cdot 3\ H_2O$)
sodium silicate (PQ Corp. N brand, 8.9% Na_2O, 28.7% SiO_2)
tetramethylammonium bromide (RSA)
aluminum sulfate (J. T. Baker, $Al_2(SO_4)_3 : 17\ H_2O$)

Batch Preparation (for 112 g dry product)

Preparation of Seed Solution [2]

(1) [30 g water + 16 g NaOH + 3.25 g alumina] reflux until a clear solution forms, then cool to room temperature and add water back to the original weight if necessary
(2) [54.4 g sodium silicate + 31.3 g water + (1)], add sodium aluminate solution slowly with mixing in a 200 mL Waring blender
(3) Age for 24 hours at room temperature[a]

Preparation of Crystallization Batch

(4) [50 g water + 19.6 g NaOH + 25.1 g alumina], reflux until clear. Cool to room temperature and add water to attain the original weight
(5) [50 g water + 40 g tetramethylammonium bromide], mix until dissolved.
(6) [396.4 g sodium silicate + 35 g water + 13.9 g (3) + (5)]. Add components sequentially with mixing in a Pyrex one-L reaction kettle with mixing. Heat mixture to 80°C
(7) [50 g water + 30 g aluminum sulfate], mix until dissolved
(8) [(6) + (4) + (7)], add sodium alumina to solution followed by alum solution with stirring at 80°C [b]
(9) Increase temperature to 100°C and stir until homogeneous

Crystallization

Vessel: one-L Pyrex reaction kettle with reflux condenser and stirrer[c]
Time: 40+ hours[d]
Temperature: 100°C
Agitation: None, except just prior to sampling

Product Recovery

(1) Vacuum filter on a Buchner funnel
(2) Wash to pH < 10
(3) Dry at 110°C
(4) Yield near quantitative on Al_2O_3

Characterization

XRD: excellent MAZ

Elemental Analyses: 0.92 Na_2O : 0.1 $(TMA)_2O$: Al_2O_3 : 7.14 SiO_2

Crystal size and Habit: barrel-shaped aggregates of needle-like crystals (2 to 3 μ long and 0.1 μ dia.)[e]

References

[1] D. E. W. Vaughan, Mater. Res. Soc. Symp. Proc. 111 (1988) 89
[2] D. E. W Vaughan, US Patent 4 178 352 (1979)

Notes

a. Stored at room temperature, this seed solution will be stable and usable for several months.
b. This formulation produces a hard gel when the alum is added making it difficult to fully homogenize. A Hobart or Kitchenaid mixer is better than a blender if available. The gel breaks up at about 80°C.
c. Alternatively, a one-L Teflon jar (Nalgene) or subdividing the gel between smaller vessels is appropriate.
d. After about 18 hours, faujasite is fully crystallized (Si / Al = 2.4). Continuing the crystallization for more than 40 hours produces fully-crystalline MAZ. It was still pure MAZ after 7 days.
e. ^{13}C NMR shows one site in the GME cage.

DropBooks

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MER — Linde W — Si(65), Al(35)

Contributed by Karl Strohmaier

Verified by P. Piccione and by Huann-Jih Lo

Type Material: $K_{11}Al_{11}Si_{21}O_{64} \cdot 20H_2O$

Method: R. M. Milton [1]

Batch Composition: 3 K_2O : 0.05 Na_2O : Al_2O_3 : 5 SiO_2 : 100 H_2O

Source Materials

deionized water
potassium hydroxide (J. T. Baker, 87.6% KOH)
alumina (Alcoa C-31, 65% Al_2O_3)
colloidal silica (duPont Ludox HS-40, 40% SiO_2)[a]

Batch Preparation (for 15 g dry product)

(1) [20 g water + 12.4 g potassium hydroxide + 5.0 g alumina], heat to a gentle boil with stirring until clear. Cool to room temperature and add water to attain the original weight
(2) [24.2 g colloidal silica +18.5 g water + (1)]. Add components sequentially with mixing in a beaker[b]

Crystallization

Vessel: 125 Teflon-lined autoclave (Parr #4748 acid digestion bomb)
Time: 48 hours
Temperature: 150°C [c]
Agitation: None

Product Recovery

(1) Vacuum filter on a Buechner funnel
(2) Wash to pH < 10
(3) Dry at 110°C
(4) Yield 15 g, near quantitative on Al_2O_3

Characterization

XRD: excellent MER, unit cell dimensions (space group I4/*mmm* - No. 139) a = 14.15Å, c = 10.03 Å
Elemental Analyses: K_2O : Al_2O_3 : 3.66 SiO_2
Crystal size and Habit: barbell-shaped aggregates (40-50 μm long and 20-30 μm dia.) of needle-like crystals.

Reference

[1] R. M. Milton, US Patent 3 012 853 (1961)

Notes

a. Available from Aldrich or Alpha.
b. Solution gels in about 5 minutes.
c. If mixture is crystallized at 100°C, a mixture of chabazite and Linde W is made.

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MFI — High-Alumina ZSM-5 — Si(93), Al(7)

Contributed by Hans Lechert and Ralph Kleinwort

Verified by A. Palmqvist and by J. Brendle and H. Kessler

Type Material: $Na_7[Al_7Si_{89}O_{192}] : wH_2O$

Method: H. Lechert, R. Kleinwort[a]

Batch Composition: 3.25 Na_2O : Al_2O_3 : 30 SiO_2 : 958 H_2O (exclusive of seeding gel)

Source Materials

distilled water
sodium hydroxide (Merck, pure)
tetrapropylammonium hydroxide (Fluka, 20% solution)
silicic acid (Merck, technical grade, SiO_2 : 0.5 H_2O)
sodium aluminate (Roth, Al_2O_3 : 1.24 Na_2O : 0.57 H_2O)

Seeding Gel Preparation[b]

(1) [710.3 g water + 13.8 g sodium hydroxide + 117.0 g TPA-OH solution], dissolve and mix thoroughly
(2) [(1) + 158.9 g silicic acid], add silica in portions under stirring. Shake the resulting mixture for one hour at ambient temperature. Age at 100°C for 16 hours

Synthesis Gel Preparation (for ~87 g product)

(1) [867.8 g water + 8.8 g sodium hydroxide + 10.3 g sodium aluminate], dissolve and mix thoroughly
(2) [(1) + 113.1 g silicic acid], add silica in portions under stirring. Shake vigorously for one hour at ambient temperature
(3) [(2) + 50 g seeding gel],[c] shake for one hour

Crystallization

Vessel: 50 mL PTFE-lined stainless steel autoclaves
Temperature: 180°C [d]
Time: 40 hours [e]
Agitation: none

Product Recovery

(1) Recover product by filtration
(2) Wash thoroughly with distilled water
(3) Dry at 105°C for 24 hours
(4) Pulverize dried product in an agate mortar [f]

Product Characterization

XRD: fully crystalline MFI;[g,h] competing phase: mordenite (at lower Si/Al ratios in the gel)
Elemental Analysis: Si/Al = 12 to 13.5[i]
Crystal Size and Habit: 6 μm crystals

References

[1] G. Bellussi, G. Perego, A. Carati, U. Cornaro, V. Fatore, in Innovation in Material Science, P. J. Grobet, W. J. Mortier (eds.), Elsevier, Amsterdam, 1988

[2] H. Kacirek, A. Meyer, German Patent 3 402 842 A1

[3] R. Kleinwort, PhD Thesis, University of Hamburg (1995)

[4] A. Nastro, C. Collella, R. Aiello, in Stud. Surf. Sci. Catal. Vol. 24, B. Drzaj, S. Hocevar, S. Pejovnik (eds.), Elsevier, Amsterdam, 1985, p 19

[5] J. M. Berak, R. Mostowcz, in Stud. Surf. Sci. Catal., Vol. 24, B. Drzaj, S. Hocevar, S. Pejovnik (eds.), Elsevier, Amsterdam, 1985

[6] W. Schwieger, K. H. Bergk, U. Haedcke, German Patent 2 83 1 26 (1990)

[7] H. P. Rieck, German Patent OS 3 242 352 (1984)

[8] P. Chu, E. J. Rosinski, European Patent Appl. 110650 (1983)

Notes

a. According to Bellussi, [1] the ZSM-5 structure crystallizes in batches of the composition: $NaAlO_2$ n[$Na_mH_{4-m}SiO_4$] pH_2O in the ranges n = 20 to 50, m = 0.1 to 0.2 and p = 400 to 500. For m < 0.1, generally amorphous products were observed. Above m = 0.2, mordenite crystallizes. For n < 20, ferrierite was found and above n = 50, zeolite Q. The Si/Al ratio in the product was nearly equal to the Si/Al in the batch. Compared to batches with template, those without template usually show a distinctly enhanced crystallization time. The enhancement is especially due to an increased induction period, leading to the conclusion that the crystallization should be carried out with the use of seeds. Another hope of the application of seeds is that the area of the formation of ZSM-5 in the crystallization field can be extended to higher m and lower n by suppressing the formation of mordenite which crystallizes preferably in that region.

b. A quite active seeding agent is obtained by carefully aging a gel giving silicalite. [2] For this gel, only a small amount of TPA-OH is necessary which does not influence the Si/Al ratio of the final product.

c. Good results have been obtained using 1-10 wt% seeding gel in the mixture.

d. Good results have been obtained at temperatures from 145° to 190°C. At 190°C, the crystallization is finished at about 10 hours.

e. The crystallization kinetics have been checked by comparison of the crystallinity with an industrial sample by X-ray. [3]

f. The final products were kept in a desiccator over saturated $CaCl_2$- solution for 24 hours before further characterization.

g. The kinetic experiments showed that the described seeding gel led to a drastically reduced induction period of crystallization and to a considerable increase in the crystallinity of MFI. This shows that the area of MFI crystallization can be extended into the range where mordenite or ferrierite has been found.

h. Crystallinity of the products was determined by comparing the sum of the peak areas between 2θ = 23.2° and 24.5° with that of a well-crystallized industrial sample which was used as a standard throughout the experiments.

i. For lower Si/Al ratios in the batch, mordenite could not be avoided. For higher Si/Al ratios in the batch, Si/Al of the products increased but remained slightly below Si/Al of the batch. Further information about the crystallization of MFI in template-free systems can be found in references [4-8].

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MFI Silicalite-1 Si(100)

Contributed by A. C. Faust and C. Schott-Darie

Verified by J. Cejka and by B. Schoeman

Type Material: $Si_{96}O_{192}F_4(TPA)_4$ (TPA = tetra-n-propylammonium)

Method: J.-L. Guth, H. Kessler, R. Wey [1]

Batch Composition: 1 SiO_2 : 0.08 (TPA)Br : 0.04 NH_4F : 20 H_2O

Source Materials

distilled water
tetrapropylammonium bromide (Fluka, 98%)
ammonium fluoride (Fluka, 98%)
silica (Degussa Aerosil 130, 99+%)

Batch Preparation (for 12 g product)

(1) [72 g water + 4.26 g tetrapropylammonium bromide + 0.296 g ammonium fluoride], stir until dissolved
(2) [(1) + 12 g silica], mix with a spatula, and then stir until homogenized. Initial pH = 6

Crystallization

Vessel: PTFE-lined autoclave
Time: 15 days[a]
Temperature: 200°C
Agitation: none

DropBooks

Product Recovery

(1) Filter, wash with distilled water
(2) Dry at 80°C
(3) Yield: 12.7 g; near 100% based on silica

Product Characterization

XRD: characteristic strong reflections at d = 11.01, 3.829, 3.806 and 3.698 Å
Elemental Analyses: $Si_{96}O_{192}F_4(TPA)_4$
Crystal Size and Habit: prisms 95 x 80 μm

Reference

[1] J.-L. Guth, H. Kessler, R. Wey, in Stud. Surf. Sci. Catal., Vol. 28, Y. Murakami, A. Iijima, J. W. Ward (eds.), Kodansha-Elsevier, Tokyo, 1986, p. 121

Note

a. Increasing NH_4F leads to a decrease in crystallization time (2 days for NH_4F/SiO_2 = 1).

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MFI [B] ZSM-5 Si(98), B(2)

Contributed by Rob de Ruiter

Verified by Z. Gabelica, by U. Deforth, and by A. Cichocki

Type Material: $Na_{0.4}(TPA)_{0.4}[B_2Si_{94}O_{192}] : wH_2O$ (TPA = tetra-n-propylammonium)

Method: R. de Ruiter, J. C. Jansen, H. van Bekkam [1]

Batch Composition: 2.1 Na_2O : B_2O_3 : 2.4 SiO_2 : 4 TPABr : 1050 H_2O

Source Materials
distilled water
silica (Aerosil 200-Degussa)
sodium hydroxide (J. T. Baker, reagent grade)
tetrapropylammonium bromide (TPABr)(CFZ Zaltbommel)
boric acid (Merck p.a.)

Batch Preparation (0.12 to 0.14 g product/35 mL autoclave)
(1) [280 g water + 2.66 g silica + 3.1 g sodium hydroxide], shake overnight at room temperature
(2) [(1) + 19.7 g tetrapropylammonium bromide], stir until dissolved
(3) [90 g water + 2.92 g boric acid], stir until dissolved
(4) [20 mL of (2) + 5 mL of (3)], mix thoroughly; initial pH ~11

Crystallization
Vessel: Teflon-lined stainless steel autoclave, 35 mL
Time: 5 days
Temperature: 180°C
Agitation: none

Product Recovery
(1) Filter and wash
(2) Yield: 60-70% on SiO_2

Product Characterization
XRD: Pure MFI, no extraneous phases
Elemental Analysis: 93.5% SiO_2, 1.25% B_2O_3, 2% TPABr, 0.25% Na_2O
Crystal Size and Habit: prismatic to lath morphology depending on boron content, the crystal thickness (in b-direction) decreases with boron content of framework

Reference

[1] R. de Ruiter, J. C. Jansen, H. van Bekkum, in Synthesis of Microporous Materials, Vol. I, M. L. Occelli, H. E. Robson (eds.), Van Nostrand Reinhold, New York, 1992, p 167

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Verified Syntheses of Zeolitic Materials. H. Robson, editor

MFI [Fe] ZSM-5 Si(96), Fe(4)

Contributed by Angelika Brückner

Verified by Y. Kiyozumi and by P. Fejes

Type Material: $Na_{0.3}(TPA)_{3.7}[Fe_4Si_{92}O_{192}] : wH_2O$ (TPA = tetra-n-propylammonium)

Method: A. Brückner, R. Lück, W. Wieker, B. Fahlke [1]

Batch Composition: 30 Na_2O : Fe_2O_3 : 30 SiO_3 : 1040 H_2O : 5 (TPA)Br : 25 H_2SO_4

Source Materials

distilled water
sulfuric acid (reagent grade, 98% H_2SO_4)
iron(III) sulfate (reagent grade, $Fe_2(SO_4)_3 \cdot 9\ H_2O$)
sodium metasilicate (reagent grade, $Na_2SiO_3 \cdot 9\ H_2O$)[a]
tetrapropylammonium bromide (TPABr) (Fluka, CH-9470 Buchs)

Batch Preparation (for ~20 g volatile-free product)

(1) [100 g water + 22 g sulfuric acid + 5.62 g iron(III) sulfate], stir until dissolved
(2) [163.4 g water + 85.26 g sodium metasilicate], stir until dissolved
(3) [(1) + (2)], add silicate slowly to iron(III) sulfate solution with good mixing
(4) [(3) + 13.31 g TPABr], mix vigorously until uniform (~ 400 rpm)

DropBooks

Crystallization

Vessel: stainless steel autoclaves
Temperature: 170°C
Time: 72 hours
Agitation: autoclaves are rotated axially

Product Recovery

(1) After cooling, filter and wash with water several times
(2) Dry over P_4O_{10}
(3) Calcine at 550°C for 4 hours to remove template

Product Characterization

XRD: ZSM-5 (only phase)
Elemental Analysis: 0.07 Na_2O : Fe_2O_3 : 48 SiO_2 : wH_2O
Crystal Size and Habit: 1-6 μm, snowball-like

Reference

[1] A. Brückner, R. Lück, W. Wieker, B. Fahlke, Zeolites 12 (1992) 380

Note

a. Al(III), a common impurity in silica sources, displaces Fe(III) from T-atom positions in MFI. [1]

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MFI [Ti] ZSM-5 Si(98.6), Ti(1.4)

Contributed by Jan H. C. van Hooff and Arjan van der Pol

Verified by D. Serrano and by Z. Gabelica

Type Material: $[Ti_{1.3}Si_{94.7}O_{192}] : wH_2O$

Method: M. Taramasso, G. Perego and B. Notari [1-3]

Batch Composition: $TiO_2 : 70\ SiO_2 : 1980\ H_2O : 30$ TPA-OH (TPA = tetra-n-propylammonium)

Source Materials

distilled water
tetraethylorthosilicate $[Si(OC_2H_5)_4]$ (Merck 800658)
tetraethylorthotitanate $[Ti(OC_2H_5)_4]$ (Merck 821083)
tetrapropylammonium hydroxide (Alfa 17456, 40% solution in water)

Batch Preparation (for 43 g product)

(1) [163.3 g tetraethylorthosilicate + 2.56 g tetraethylorthotitanate], mix at 35°C
(2) [(1) + 170 g tetrapropylammonium hydroxide (40% solution)], add slowly at 0°C to prevent hydrolysis
(3) Heat at 80°C to evaporate ethanol
(4) Add water to restore initial volume; final pH 12.2

Crystallization

Vessel: 500 mL stirred autoclave
Temperature: 175°C
Time: 2 days
Agitation: 120 rpm

Product Recovery

(1) Centrifuge to recover solids and wash with water (three times)
(2) Dry at 120°C
(3) Heat in air to 550°C (heating rate 5°C/min.) and hold at 550° for 3 hours
(4) Yield: ~ 90% on SiO_2

Product Characterization

XRD: orthorhombic MFI (only crystalline phase)
Elemental Analysis: 1.37 mol% Ti (72 SiO_2/TiO_2 by AAS)[a]
Crystal Size and Habit: 0.3 μm cubes (SEM)

References

[1] M. Taramasso, G. Perego, B. Notari, US Patent 4 410 501 (1983)
[2] A. J. H. P. van der Pol, J. H. C. van Hooff, Appl. Catal. 92 (1992) 93
[3] J. A. Martens, P. Buskens, P. A. Jacobs, A. van der Pol, J. van Hooff, P. J. Kooymann, H. van Bekkum, Appl. Catal. 99 (1993) 71
[4] A. Tuel, Y. Ben Taarit, Zeolites 14 (1994) 272

Note

a. No extra-framework TiO_2 can be observed by IR or UV-VIS. No IR bands around 700 cm^{-1} and no UV-VIS bands above 250 nm were observed [4].

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MFI [Ti, Al] ZSM-5 Si(97.5), Ti(1.3), Al(1.2)

Contributed by D. P. Serrano, G. Ovejero, R. Van Grieken and J. A. Melero

Verified by M. Anderson and by J. Rocha and A. Ferreira

Type Material: $H_{1.2}[Al_{1.17}Ti_{1.23}Si_{93.6}O_{192}] : wH_2O$

Method: G. Ovejero, R. Van Grieken, M. A. Uguina, D. P. Serrano, J. A. Melero [1]

Batch Composition: $1\ TiO_2 : 0.25\ Al_2O_3 : 40\ SiO_2 : 216\ H_2O : 7.44$ (TPA)OH
(TPA = tetra-n-propylammonium)[a]

Source Materials

tetraethylorthosilicate [Alfa, $Si(OC_2H_5)_4$]
hydrochloric acid (0.2 N) (reagent grade)
isopropyl alcohol for analysis (Panreac)
aluminum isopropoxide, [Aldrich, $Al(OC_3H_7)_3$]
tetrapropylammonium hydroxide (TPAOH)
[Alfa, 40 wt% $(C_3H_7)_4NOH$ in water]
titanium tetrabutoxide [Alfa, $Ti(OC_4H_9)_4$]

DropBooks

Batch preparation (for ~ 2.9 g dried cogel)

A. Acid hydrolysis-condensation

(1) [8 g tetraethylorthosilicate + 5 g hydrochloric acid (0.2 N)], mix at room temperature for 45 minutes
(2) [2.5 g isopropyl alcohol + 0.098 g aluminum isopropoxide], mix until dissolved
(3) [(1) + (2)], add (2) to (1) dropwise. Mix at room temperature for 45 minutes.
(4) [4 g TPAOH (40 wt%) + 4 g H_2O], mix
(5) [(3) + 0.75 g (4)], add 20 wt% TPAOH slowly at room temperature. Stir at 0°C for 15 minutes
(6) [0.327 g titanium tetrabutoxide + 2 g isopropyl alcohol], mix until homogeneous
(7) [(5) + (6)], add (6) to (5) slowly at 0°C. Stir at 0°C for an additional 20 minutes

B. Basic Gelation:

(8) [(7) + approximately 1.9 g (4)], add 20 wt% TPAOH slowly at room temperature; mix until gelation
(9) Dry overnight at 110°C to remove alcohol and water. Grind to give a powdered material
(10) [(9) + approximately 4.6 g (4)], impregnate the dried and powdered cogel to incipient wetness with 20 wt% TPAOH. Charge to autoclaves

Crystallization

Vessel: Teflon-lined autoclaves (50 mL)
Time; 24 hours
Temperature: 170°C
Agitation: none

Product Recovery

(1) Centrifuge to recover crystalline product; wash with double-distilled water (three times)
(2) Dry overnight at 110°C
(3) Calcine in air at 550°C (heating rate 5°C/minutes and hold at 550°C for 5 hours)
(4) Yield; ~ 95% on SiO_2

Product Characterization

XRD: MFI structure, orthorhombic
Elemental Analysis: $SiO_2/TiO_2 = 76$, $SiO_2/Al_2O_3 = 160$ (by XRF)[b,c]
Crystal Size and Habit: 0.4-0.5 μm, cuboid shape

References

[1] G. Ovejero, R. Van Grieken, M. A. Uguina, D. P. Serrano, J. A. Melero, Catal. Lett. 41 (1996) 69
[2] G. Bellussi, A. Carati, M. G. Clerici, A. Esposito, Stud. Surf. Sci. Catal. 63 (1991) 421
[3] L. Forni, M. Pellozi, A. Giusti, G. Fornasari, R. Millini, J. Catal. 122 (1990) 44
[4] A. Thangaraj, R. Kumar, S. Sivasanker, Zeolites 12 (1992) 135
[5] D. Trong On, S. Kaliaguine, L. Bonneviot, J. Catal. 157 (1995) 235
[6] F. Geobaldo, S. Bordiga, A Zecchina, E. Gianello, G. Leofanti, G. Petrini, Catal. Lett. 16 (1992) 109

Notes

a. Ti and trivalent metal ions, Al+3, Ga+3, Fe+3 and B+3, can be co-incorporated into ZSM-5 by conventional methods based on hydrothermal crystallization of a liquid gel obtained from respective alkoxides hydrolyzed in basic medium. [2-5]
b. By DR UV-VIS, adsorption around 330 nm is not detected either in the sample or in the cogel, showing the absence of bulk TiO_2 phases. [6]
c. By ^{29}Si and ^{27}Al MAS-NMR, atoms are located in tetrahedral environments in the starting cogel and in the synthesized sample.

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MOR Mordenite Si(90), Al(10)

Contributed by Wha Seung Ahn

Verified by G. Price, by K. Satya Narayana Reddy, and by Yan Sun

Type Material: $Na_5[Al_5Si_{43}O_{96}] : w\ H_2O$

Method: G. J. Kim, W. S. Ahn [1]

Batch Composition: $6\ Na_2O : Al_2O_3 : 30\ SiO_2 : 780\ H_2O$

Source Materials

distilled water
sodium hydroxide (Junsei Co., 95% NaOH)
sodium aluminate (Junsei Co., 32.6% Na_2O, 35.7% Al_2O_3)
silica powder (Zeosil from Kofran Co., 91.8% SiO_2, 8.2% H_2O)[a]

Batch Preparation (for 56 g dry product)

(1) [40 g water + 19 g sodium hydroxide], stir until dissolved
(2) [(1) + 14.3 g sodium aluminate], stir until dissolved
(3) [(2) +645 g water], mix
(4) [(3) + 98.2 g silica], stir for 30 minutes

DropBooks

Crystallization

Vessel: Teflon-lined stainless steel autoclave
Incubation: none[b]
Temperature: 170°C
Time: 24 hours[c]

Product Recovery

(1) Filter and wash to pH < 10
(2) Dry at 100°C
(3) Yield: near 100% on Al_2O_3

Product Characterization:

XRD: 100% mordenite, characteristic peaks at d = 3.45, 3.97, 9.02, 3.27 and 3.21 Å; competing phases: quartz, analcime, gismondine
Elemental Analysis: $Na_2O : Al_2O_3 : 17.2\ SiO_2$

Crystal Size and Habit: irregular spherical to prismatic, ~ 5 μm[d]

Reference

[1] G. J. Kim, W. S. Ahn, Zeolites 11 (1991) 745

Notes

a. Sodium silicate can also be used as a silica source, but crystallization rates are lower.
b. Incubation is not required when using silica powder as SiO_2 source; aging at room temperature resulted in larger crystals but lower crystallization rates.
c. Seeding with 5 wt% mordenite in the reaction batch substantially improved the crystallization rate.
d. Typically needle-shaped crystals, but siliceous crystals can be plate or flat prismatic shape.

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MTN ZSM-39 Si(100)

Contributed by Valentin Valtchev

Verified by S. Ernst and by A. Iwasaki

Type Material: $(SiO_2)136 : q\ R$; $q \approx 10$, (R = TMA^+ and TrMA)[a]

Method: I. Vergilov, V. Valtchev [1]

Batch Composition: 15 Na_2O : 16 TrMA : 16 (TMA)Cl : 55 SiO_2 : 3387 H_2O : 10 H_2SO_4[b,c]

Source Materials

bidistilled water
sodium silicate (Riedel de Haen, 63% SiO_2, 18% Na_2O, 18% H_2O)
sulfuric acid (98% H_2SO_4)
trimethylammonium (TrMA) chloride (Merck, 98% TrMA·HCl)
tetramethylammonium (TMA) chloride (Merck, > 98% (TMA)Cl

Batch Preparation (for 30 g dry product)

(1) [300 g water + 52.5 g sodium silicate], heat and stir until dissolved [d]
(2) [150 g water + 10.7 g sulfuric acid]
(3) [(1) + (2)], mix thoroughly
(4) [15.29 g trimethylammonium chloride + 17.54 g tetramethylammonium chloride + 150 g water], mix thoroughly
(5) [(3) + (4)], mix thoroughly; pH 9.2 to 9.5

Crystallization

Vessel: stainless steel or Teflon jar
Time: 12 to 14 days
Temperature: 200°C
Agitation: none

Product Recovery

(1) After crystallization, pH 10.5
(2) Filter to recover solids, and wash with hot water
(3) Dry at ambient temperature (drying at 90-110°C acceptable)
(4) Yield: 88% based on silica

Characterization

XRD: MTN only crystalline phase,[e] a_o = 19.39 Å, single crystal structure refinement [2];
competing phases: NU-1 (when gel contains aluminum), quartz (when pH of starting gel > 11.5)
Elemental Analysis: 0.0018 $Na_2O \cdot SiO_2$[f]
Crystal Size and Habit: octahedral morphology, 100 to 200 nm dia. [1]

References

[1] I. Vergilov, V. Valtchev, Zeolites 11 (1991) 387
[2] J. Macicek, V. Valtchev, G. Kirov, in Collected Abstracts, 14th Congress and General Assembly Int. Union of Crystallography, H. C. Freeman (ed.), Lamb Printers, Perth, Australia, 1987, C-134

Notes

a. Crystalline product is 7.4 wt% TMA^+ and TrMA by thermal analysis.
b. With TMA^+ only, complex crystal twins are formed.
c. H_2O includes water from sodium silicate, sulfuric acid and added water.
d. Sodium silicate solution must be heated and stirred until converted to a clear solution.
e. XRD patterns of as-synthesized product and product after 600°C calcination do not differ significantly.
f. Analysis of ZSM-39 calcined for 1 hour at 950°C in air gave 94.7% SiO_2, 0.17% Na_2O, and a remainder, probably consisting of carbonaceous material and water.

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MTT ZSM-23 Si(97), Al(3)

Contributed by Stefan Ernst

Verified by R. Ravishankar and by Wha-Seung Ahn

Type Material: $Na[AlSi_{23}O_{48}] \cdot wH_2O$ $(w \approx 4)$

Method: S. Ernst, R. Kumar, J. Weitkamp [1]

Batch Composition: $20.6Na_2O : Al_2O_3 : 100SiO_2 : 4610H_2O : 46.2Pyrr : 18.8\ H_2SO_4$

Source Materials

demineralized water
sodium hydroxide, reagent grade (Riedel-de Haën)
pyrogenic silica (Cab-o-Sil M5)[a]
pyrrolidine (Pyrr), (Fluka)
aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$, Fluka)
sulfuric acid (96 wt% H_2SO_4, Fluka)

Batch Preparation (for 14 g product)[b]

(1) [195.8 g water + 4.40 g sodium hydroxide], mix until dissolved
(2) [(1) + 16.5 g silica], add silica to solution (1) over the course of ~5 minutes under continuous stirring
(3) [24.4 g water + 8.81 g pyrrolidine + 1.79 g aluminum sulfate], mix until dissolved
(4) [(2) + (3)], add solution (3) to solution (2) with good mixing
(5) [(4) + 4.33 g sulfuric acid], add acid dropwise with stirring; final gel pH = 12.6

Crystallization

Vessel: stainless steel autoclave (300 mL)[c]
Temperature: 180°C
Time: 50 hours
Agitation: autoclaves are rotated ~ 30/minutes

Product Recovery

(1) Cool and filter
(2) Wash extensively with demineralized water
(3) Dry at 100°C for 16 hours
(4) Yield: approx. 14 g

Product Characterization

XRD: MTT (only crystalline phase), competing phases: MFI (contaminated autoclave) cristobalite (occasional overheating, or pH too high)
Elemental Analysis: $SiO_2/Al_2O_3 = 78$ (AES/ICP)[d]
Crystal Size and Habit: bundles of needles[e]

Reference

[1] S. Ernst, R. Kumar, J. Weitkamp, in Zeolite Synthesis, Am. Chem. Soc. Symposium Series 398, M. Occelli, H. Robson (eds.), 1989, pp 560-573

Notes

a. Cab-O-Sil M5 must be used; other silica sources, such as silica sol or sodium silicate, lead to different products.
b. The synthesis has been successfully scaled up to a 5 liter autoclave (stirring rate: 120/minutes, yield: 250 g).
c. The crystallization vessels have to be cleaned very thoroughly in order to avoid seeding effects from residual crystallites of ZSM-5, for example.
d. With pyrrolidine as template, the molar ratio can be varied between 70 and 150.
e. Platelet-like ~1 μm can be synthesized using C_7-diquat $[(CH_3)_3N\text{-}(CH_2)_7\text{-}N(CH_3)_3]Br_2$ as template. [1]

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MTW ZSM-12 Si(97), Al(3)

Contributed by Girolamo Giordano

Verified by Nguyen Huu Phu, by A. Souza de Araujo, and by G. Kühl

Type Material: $Na_{0.5}(MTEA)_{1.3}[Al_{0.8}Si_{27.2}O_{56}] : 0.6\ H_2O$ (MTEA = methyltriethylammonium)

Method; S. Ernst, P. A. Jacobs, J. A. Martins, J. Weitkamp [1], P. Chu, G. H. Kühl [2]

Batch Composition: $10\ Na_2O : Al_2O_3 : 100\ SiO_2 : 2000\ H_2O : 20$ MTEA Br

Source Materials

distilled water
sodium hydroxide (Carlo Erba RPE, 99+% NaOH)
aluminum hydroxide hydrate [$Al(OH)_3$] (Aldrich)
methyltriethylammonium bromide [MTEA Br] (Fluka)
precipitated silica (BDH, 99+% SiO_2)

Batch Preparation (for ~ 2.5 g product)

(1) [9 g distilled water + 0.4 g sodium hydroxide + 0.078 g aluminum hydroxide hydrate], stir until dissolved
(2) [9 g distilled water + 1.96 g MTEA Br], stir until dissolved
(3) [(1)+ (2)], stir until homogenized
(4) [(3) + 3 g precipitated silica], stir for 1 hour at room temperature and seal in the reactor

Crystallization

Vessel: Teflon-lined autoclave, 20 mL
Time: 6 days
Temperature: 140°C
Agitation: none

Product Recovery

(1) Cool to room temperature and filter to recover solids
(2) Wash with distilled water until filtrate pH = 9
(3) Dry at 105°C

Product Characterization

XRD: MTW only crystalline phase; competing phases: MFI (high alumina), cristobalite (high temperature or high pH)
Elemental Analyses: $0.66\ Na_2O : Al_2O_3 : 66.7\ SiO_2 : 1.5\ H_2O : 1.58\ (MTEA)_2O$
Crystal Size and Habit: rice-grain shaped, length 5 μm

References

[1] S. Ernst, P. A. Jacobs, J. A. Martens, J. Weitkamp, Zeolites 7 (1987) 458
[2] P. Chu, G. H. Kühl, US Patent 4 452 769 (1983)
[3] A. Katovic, G. Giordano, Chem. Express 6 (1991) 969

Note

a. MTW zeolite can also be obtained when tetraethylammonium bromide (TEA Br) substitutes for MTEA Br in the hydrogel described in the Batch Composition section. In this case spheroidal crystals of about 0.6 μm diameter are obtained. [3]

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MTW [Ga] ZSM-12 Si(93), Ga(7)

Contributed by Susan Lambert

Verified by K. Reddy and by M. Mertens

Type Material: $Na_2[Ga_2Si_{26}O_{56}] : 4\ H_2O$

Method: S. L. Lambert [1]

Batch Composition: $4.5\ Na_2O : Ga_2O_3 : 52.4\ SiO_2 : 13.7$ TEMA Br : $867\ H_2O$
(TEMA = triethylmethylammonium)

Source Materials
deionized water
sodium hydroxide (Mallinkrodt dry pellets, > 98.5% NaOH)
gallium oxide (Alfa, 99.99%)
triethylmethylammonium bromide (TEMA Br) (Fluka, purum)
silica sol (Dupont Ludox AS-40, 40% SiO_2)[a]

Batch Preparation (for 13 g dry product)
(1) [21.72 g NaOH + 37.04 g water + 11.37 g Ga_2O_3], heat in a closed pressure vessel (Teflon-lined Parr acid digestion bomb) at 110°C for 23 hours
(2) [4.65 g of solution (1) + 29.22 g water + 10.78 g TEMA Br], stir until dissolved
(3) [(2) + (31.47 g silica sol + 11.63 g H_2O)], add diluted silica sol to (2) with stirring using an eye dropper over course of 15 min. Batch pH 13-14[b]

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Crystallization
Vessel: two Teflon-lined Parr acid digestion bombs (125 mL)
Time: 20 days[c]
Temperature: 150°C
Agitation: none

Product Recovery
(1) Supernatant liquid pH 12.5
(2) Filter and wash with 600 mL distilled water
(3) Dry at 100°C
(4) Yield: 13.64 g white solids (12.25 g volatile free), 91% recovery on SiO_2 or 87% on Ga_2O_3

Product Characterization
XRD: MTW framework by comparison to ZSM-12 crystallinity reference, best is [Al] MTW.
Minor impurity: cristobalite; no other phases present
Elemental Analyses (volatile-free): 93.4% SiO_2, 5.35% Ga_2O_3, 0.62% Na_2O, 0.14% Al_2O_3. Loss on ignition at 900°C: 10.17%[d]
Molar Composition: $0.35\ Na_2O : 0.05\ Al_2O_3 : Ga_2O_3 : 54.4\ SiO_2 : 22\ H_2O$[e]

Reference

[1] S. L. Lambert in Proceedings of the 9th International Zeolite Conference, R. von Ballmoos, J. B. Higgins, M. M. J. Treacy (eds.), Butterworth-Heinemann, London, 1993, p. 223

Notes

a. Dupont's Ludox HS-40 is an acceptable substitute.
b. pH values were measured with ColorpHast pH indicator paper (range 5-10 or 7.5-14, from E. M. Science, Gibbstown, NJ, USA)
c. Crystallinity vs. (Al) ZSM-12 reference: 70% after 16 days, 88% after 18 days, 90% after 20 days. The crystallization proceeds more rapidly as the amount of gallium in the synthesis batch is reduced.
d. Template burnout occurs at 460°C in air.
e. By ^{29}Si MAS NMR, Si/(Ga + Al) = 14; excess SiO_2 by elemental analysis is attributed to amorphous silica. ^{71}Ga static NMR: one symmetrical Ga line at 158.5 ppm (ref. $Ga(NO_3)_3$).

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MWW MCM-22 Si(94), Al(6)

Contributed by Avelino Corma

Verified by J. Weitkamp and by N. Kumar

Type Material: $Na_{0.08}[Al_4Si_{68}O_{144}] : (C_6H_{12}NH)_{10.8}$ [1][a]

Method; A. Corma, C. Corell, J. Pérez-Pariente [1]

Batch Composition: 2.7 $Na_2O : Al_2O_3 : 30\ SiO_2 : 1347\ H_2O : 15$ HMI[b] (HMI = hexamethyleneimine)

Source Materials

deionized water
sodium aluminate (Carlo Erba, 56% Al_2O_3, 37% Na_2O)
sodium hydroxide (98% NaOH)
hexamethyleneimine $C_6H_{12}NH$ (Aldrich, 99% HMI)
silica (Degussa, Aerosil 200, or Cab-O-Sil M5)

Batch Preparation (for 12.8 g dry product)[c]

(1) [124.20 g water + 0.92 g sodium aluminate + 0.60 g sodium hydroxide], stir until dissolved [d]
(2) [(1) + 7.61 g hexamethyleneimine], mix thoroughly[e]
(3) [(2) + 9.23 g silica], mix thoroughly[f]

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Crystallization

Vessel: PTFE-lined stainless steel autoclaves
Time: 7 days
Temperature: 150°C
Agitation: 60 rpm

Product Recovery

(1) Dilute the reaction mixture with distilled water
(2) Filter and wash with distilled water
(3) Dry at 100°C overnight
(4) Yield; 99% based on alumina

Product Characterization

XRD: MCM-22 [2]; competing phases: FER (when crystallized under static conditions), ZSM-5 (when gel $SiO_2/Al_2O_3 > 100$), ZSM-12 (when gel $SiO_2/Al_2O_3 > 200$)

Elemental Analysis: 0.02 $Na_2O : Al_2O_3 : 34\ SiO_2$

Crystal Size and Habit: small thin platelets occasionally forming spherical aggregates of 6-8 μm [g]

References

[1] A. Corma, C. Corell, J. Pérez-Pariente, Zeolites 15 (1995) 2
[2] M. K. Rubin, P. Chu, US Patent 4 954 325 (1990)

Notes

a. Missing cations assumed to be protonated HMI.
b. H_2O includes water from sodium aluminate and added water.
c. Use polypropylene vessel and vigorous stirring for 30 minutes.
d. Clear solution
e. Slightly yellow clear solution
f. White and fluid gel
g. Toluene sorptive capacity at 0.1 KPa, 42°C : 10.07 mmol/g. The sample was heated in oxygen flow (30 cm^3/min^{-1}) up to 500°C and outgassed overnight at 500°C in a vacuum better than 1 mPa.

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NAT [Ga] Natrolite Si(62), Ga(38)

Contributed by Mario Occelli

Verified by J. Buhl and by R. Aiello

Type Material: $(NaK_8R_6)[Ga_{15}Si_{25}O_{80}] \cdot wH_2O$ (R = benzyl trimethylammonium (BTMA))

Method: M. L. Occelli, E. Goldish, H. Eckert [1]

Batch Composition: 5.30 Na_2O : 2.21 K_2O : 2.12 R_2O : Ga_2O_3 : 12.54 SiO_2 : 298 H_2O : 31.4 CH_3OH

Source Materials

deionized water
sodium hydroxide, reagent grade (~97% NaOH)
potassium hydroxide, reagent grade (85% KOH)
gallium oxide (99.99% Ga_2O_3)
sodium silicate (PQ N-brand, 29,9% SiO_2, 10.0% Na_2O)
benzyl trimethyl ammonium hydroxide (Excel Co., 40% in methanol)

Batch Preparation

(1) [50 g water + 9.92 g sodium hydroxide + 29.0 g potassium hydroxide] mix until dissolved
(2) [(1) + 18.7 g gallium oxide], stir at the boiling point until the solution clears
(3) [(2) +50 g water], mix and cool to ambient temperature[a]
(4) [(3) + 167.2 g BTMA·OH solution]
(5) [251.3 g sodium silicate + 274.3 g water] mix for 4 hours
(6) [(5) + (4)], add gallate mixture dropwise to the vigorously stirred, diluted sodium silicate; stir for 10 hours at ambient temperature

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Crystallization

Vessel: Teflon-lined, stirred autoclave
Incubation: 10 h at ambient temperature with stirring.
Temperature: 125±2°C
Time: 7 days
Agitation: 100 rpm

Product Recovery

(1) Filter and wash to pH < 10
(2) Dry at 110°C
(3) Yield: near 100% on Ga_2O_3

Product Characterization

XRD: NAT; no other crystalline phases or amorphous material observed
Elemental Analyses: $Ga_2O_3 \cdot 3.28\ SiO_2 \cdot 0.11\ Na_2O \cdot 0.56\ K_2O \cdot 0.39\ (BTMA)_2O$

Crystal Size and Habit: Anisotropic columns 10-20 μm long with an almost square cross section often bounded at both ends by pyramids. Twinning and intergrowths are common

Reference

[1] M. L. Occelli, E. Goldish, H. Eckert, in Stud. Surf. Sci. Catal. 84, J. Weitkamp, H. G. Karge, H. Pfeifer, W. Hölderich (eds.), 1994, p. 597

Note

a. Diluted gallate solution must be clear.

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OFF — Linde Type T — Si(78), Al(22)

Contributed by Andrzej Cichocki

Verified by S. Khvoshchev and M. Shubaeva, by J. Warzywoda, by J. Parise, M. Kleinsorge and S. Park, and by Conghua Liu

Type Material: $Na_{2.9}K_{5.4}[Al_{8.3}Si_{27.7}O_{72}] \cdot wH_2O$ (w ~7)

Method: A. Cichocki, P. Koscielniak [1, 2]

Batch Composition: 4.18 Na_2O : 1.25 K_2O : Al_2O_3 : 16.5 SiO_2 : 175 H_2O

Source Materials
- distilled water
- sodium hydroxide (97% NaOH)
- potassium hydroxide (86% KOH)
- silica sol (Rudniki Chemical Works, 29.5% SiO_2, 0.2% Na_2O)
- sodium aluminate solution (26.6% Al_2O_3, 19.6% Na_2O) = $NaAlO_2$

Batch Preparation (for 14 g dry product)
(1) [9.57 g water + 4.67 g sodium hydroxide + 3.24 g potassium hydroxide], dissolve and cool to room temperature
(2) [67.0 g silica sol + (1)], mix in a porcelain mortar and stir for 2 minutes [a]
(3) [(2) + 7.64 g sodium aluminate solution], add $NaAlO_2$ drop by drop to the stirred silicate over a 10 min. interval and continue stirring for 20 minutes

Crystallization
- Vessel: stainless steel autoclave, 120 cm^3 capacity
- Aging: 24 h at room temperature
- Temperature: 140°C
- Time: 7 days
- Agitation: none

Product Recovery
(1) Cool; transfer the reaction mixture to a mortar and grind
(2) Filter and wash in a Buechner funnel until pH of the filtrate is ~ 10
(3) Dry at 110°C
(4) Equilibrate in laboratory air for a few days
(5) Yield: near 95% on Al_2O_3 and 41.5% on SiO_2 [b]

Product Characterization
- XRD: pure OFF;[c] competing phases: PHI, CHA, LTL[d]
- Elemental Analysis: 0.35 $Na_2O \cdot 0.65\ K_2O \cdot Al_2O_3 \cdot 6.65\ SiO_2$
- Crystal Size and Habit: rods and "bones" type crystals ~ 9 μm long on average (longest ~22 μm)

References

[1] A. Cichocki, P. Koscielniak, M. Michalik, M. Bus, Zeolites 18 (1997) 25
[2] A. Cichocki, P. Koscielniak, Micropor. Mesopor. Mater. 29 (1999) 369
[3] A. Cichocki, Zeolites 11 (1991) 758
[4] R. Aiello, R. M. Barrer, J. Chem. Soc. 1970 (A), 1470

Notes

a. The use of a porcelain mortar gives a good mix of the reagents, particularly aluminate and silica sol.

b. 39.9% of the sum of Na_2O, K_2O, Al_2O_3 and SiO_2 masses introduced into the reaction mixture. Synthetic erionite with SiO_2/Al_2O_3 = 6.55 forms from a reaction mixture of composition 8.09 Na_2O : 2.38 K_2O : Al_2O_3 : 27.0 SiO_2 : 448 H_2O when crystallization is carried out in a stainless steel autoclave at the temperature 373 K and time 7 days, but the yield is reduced to 22.5%. This composition differs slightly from that given in ref. [3] where NaOH and KOH were assumed 100%.

c. The Na/K-system synthetic product shows domains of erionite and offretite in a single crystal. The XRD pattern agrees with natural offretite (PDF), but the product shows adsorption properties of erionite. Unfaulted erionite crystallized in the Na/Me_4N-system. [4]

d. Formation of PHI is favored by decreasing relative alkalinity (OH^-/SiO_2). Decreasing the temperature of crystallization favors CHA. Increasing relative alkalinity leads to formation of LTL.

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Verified Syntheses of Zeolitic Materials. H. Robson, editor.

OFF Offretite Si(79), Al(21)

Contributed by Hans Lechert

Verified by M. Mertens and by R. Russu

Type Material: $Na_{0.2}K_{0.9}[Al_4Si_{14}O_{36}] : wH_2O$[a]

Method: H. Lechert, H. Weyda [1]

Batch Composition: 3.0 Na_2O : 1.0 K_2O : Al_2O_3 : 20.8 SiO_2 : 1.73 (TMA)Cl : 324 H_2O[b]
(TMA = tetramethylammonium)

Source Materials
distilled water
sodium hydroxide, reagent grade (99+% NaOH)
aluminum tri-isopropylate [$Al(OC_3H_7)_3$]
potassium hydroxide, reagent grade (87% KOH)
silica (Merck, precipitated and dried, 87% SiO_2)
tetramethylammonium chloride [Merck, $N(CH_3)_4Cl$]

Batch Preparation (for 64 g dry product)
(1) [28.1 g water + 16.8 g sodium hydroxide], mix until dissolved
(2) [(1) + 42.5 g aluminum tri-isopropylate], stir at 100°C and evaporate to reduce to 42.0 g
(3) [(2) + 58 g water], stir and cool to ambient temperature; dilute to 100 g total
(4) [379.3 g water + 8.4 g sodium hydroxide + 13.4 g potassium hydroxide], mix until dissolved
(5) [(4) + 149.4 g silica], mix for 30 minutes
(6) [(5) + (3)], mix for 30 minutes
(7) [(6) + 126.4 g water], mix for 30 minutes
(8) [(7) + 19.7 g tetrametylammonium chloride], mix for 30 minutes

Crystallization
Vessel: Teflon-lined autoclave
Temperature: 160°C
Time: 20 hours
Agitation: none

Product Recovery
(1) Centrifuge
(2) Wash to near neutrality
(3) Dry at 100°C
(4) Yield: near 100% on Al_2O_3

Product Characterization
XRD: Strong OFF, no extraneous phases; competing phases: erionite,[c] Zeolite P (GIS), analcime
Elemental Analysis: 0.10 Na_2O : 0.46 K_2O : Al_2O_3 : 7.72 SiO_2[d]
Crystal Size and Habit: "rice grains," length 5-10 μm[e]

Reference

[1] H. Lechert, H. Weyda, in Synthesis of Microporous Materials, Vol. I, M. L. Occelli, H. Robson (eds.), Van Nostrand Reinhold, New York, 1992, p. 77

Notes

a. Missing cations assumed to be TMA^+ or (after calcination) H^+.

b. OFF can be obtained without template in the temperature range 87-107°C with a gel (6.2 Na_2O : 3.5 K_2O : Al_2O_3 : 25 SiO_2 : 390 H_2O), but slight deviations from this composition give appreciable amounts of erionite or gismondine. At higher temperatures Zeolite P (GIS) and analcime co-crystallize with offretite.

c. ERI can be distinguished from OFF in the XRD pattern by lines at d = 9.13, 5.37, 4.60, 4.17, 3.28, and 2.82 Å.

d. The template content of the product is quite low (less than one TMA^+ per UC).

e. At 190°C, pure erionite can be obtained from a batch composition: 8.0 Na_2O : 1.7 K_2O : Al_2O_3 : 24 SiO_2 : 1.7 TMACl : 410 H_2O. At this temperature the offretite is needles of about 1 μm diameter x 25 μm long. At crystallization times longer than 4 hours at 190°C, an increasing amount of analcime is observed.

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Verified Syntheses of Zeolitic Materials. H. Robson, editor.

OFF [Ga] Offretite Si (65), Ga (35)

Contributed by Mario Occelli

Verified by F. Machado and by S. Iwamoto

Type Material: $K_{2.2}Na_{0.1}(TMA)_{4.1}Ga_{6.4}Si_{11.6}O_{36} : wH_2O$ (TMA = tetramethylammonium)

Method: M. L. Occelli [1]

Batch Composition: 2.25 K_2O : 1.61 Na_2O : 0.5 $(TMA)_2O$: Ga_2O_3 : 11.7 SiO_2 : 250 H_2O : 1.0 HCl

Source Materials

deionized water
sodium hydroxide, reagent grade (~97% NaOH)
potassium hydroxide, reagent grade (~87% KOH)
gallium oxide (99.99%)
silica sol (Dupont HS-40, 39% SiO_2, 0.5% Na_2O)
tetramethylammonium chloride [99+% (TMA)Cl]

Batch Preparation

(1) [50 g water + 12.0 g sodium hydroxide + 29.0 g potassium hydroxide], mix until dissolved; heat to boiling
(2) [(1) + 18.7 g gallium oxide], stir at boiling point until a clear solution is obtained
(3) [(2) + 30 g water], mix and cool to ambient temperature[a]
(4) [20 g water + 11.0 g (TMA)Cl], mix until dissolved
(5) [(3) + (4)], mix thoroughly
(6) [180.3 g silica sol + 234.8 g water], mix for 4 hours
(7) [(6) + (5)], add gallate mixture dropwise to the vigorously-stirred diluted silica sol. Continue stirring in a round-bottomed flask for 10 hours

Crystallization

Vessel: 1000 mL round bottomed flask with agitator and reflux condenser
Incubation: 10 h at ambient temperature with stirring
Temperature: 98°C[b]
Time: 3 days[c]
Agitation: Continue stirring until temperature reaches 98°C, then discontinue stirring for balance of crystallization period

Product Recovery

(1) Filter and wash with deionized water until pH < 10
(2) Dry at 110°C
(3) Yield: near 100% on Ga_2O_3

Product Characterization

XRD: OFF, no other crystalline products or amorphous material detected
Elemental Analyses: 49.5% SiO_2, 42.2% Ga_2O_3, 7.2% K_2O, 1.1% Na_2O[d]

References

[1] M. L. Occelli, US Patent 5 133 951 (1992)
[2] M. L. Occelli, H. Eckert, C. Hudalla, A. Auroux, P. Ritz, P. S. Iyer, Micropor. Mater. 10 (1997) 123-135
[3] M. L. Occelli H. Eckert, C. Hudalla, A. Auroux, P. Ritz, P. S. Iyer, in Proceedings of the 11th International Zeolite Conference, Seoul, Korea, Hakze Chon, Son-Ki Ihm (eds.), Elsevier, Amsterdam, 1997, p 1981
[4] M. L Occelli, H. Eckert, P. S. Iyer, P. Ritz, in Synthesis of Porous Materials, M. L. Occelli, H. Kessler (eds.), Marcel-Dekker (1997), p. 283

Notes

a. Diluted Na,K gallate solution must be clear.
b. Stirring is continued as temperature is increased to 98°C, then discontinued for the remainder of the crystallization treatment.
c. Methods to reduce crystallization time are given in ref. [1].
d. After calcination in nitrogen for 2 hours at 500°C followed by calcination in air for 10 hours at 550°C; the BET surface area was 404 m^2/g. Characterizations of similar gallium offretites are given in references [2-4].

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PAU ECR-18 Si(76), Al(24)

Contributed by David Vaughan

Verified by P. Piccione and by B. Subotic´

Type Material: $(Na_{82}K_{66}TEA_{16})[Al_{164}Si_{508}O_{1344}] : wH_2O$ (TEA = tetraethylammonium)

Method: D. E. W. Vaughan, K. G. Strohmaier [1,2]

Batch Composition: 0.4 K_2O : 0.6 Na_2O : 1.4 $(TEA)_2O$: Al_2O_3 : 9 SiO_2 : 0.3 Na_2SO_4 : 140 H_2O

Source Materials

deionized water
potassium hydroxide (J. T. Baker, >99% KOH · 0.5 H_2O)
sodium hydroxide (J. T. Baker, ~99% NaOH)
alumina (Alcoa C-31, >99% Al_2O_3 · 3 H_2O)
silica sol (Dupont HS-40, 40% SiO_2, 0.4% Na_2O)
tetraethylammonium hydroxide (SACHEM, 35% $N(C_2H_5)_4OH$)
aluminum sulfate (reagent grade, > 99% $Al_2(SO_4)_3 \cdot 17H_2O$)

Batch Preparation (for 20 g dry product)

(1) [8.0 g water + 1.79 g potassium hydroxide + 2.8 g sodium hydroxide + 5.1 g alumina], reflux until a clear solution is obtained; cool to room temperature. Replace water lost by evaporation
(2) [10 g aluminum sulfate + 10 g water], mix and warm if necessary to make a solution
(3) [49.7 g silica sol + 43.3 g tetraethylammonium hydroxide + (1) + 5.29 g (2) + 19 g water], add sequentially with mixing in a beaker

Crystallization

Vessel: 125 mL Teflon jar (Nalgene)
Incubation: 3 days at room temperature
Time: 12 to 16 days[a]
Temperature: 100°C
Agitation: none

Product Characterization

XRD: excellent PAU
Elemental Analysis: 0.4 K_2O : 0.5 Na_2O : 0.1 $(TEA)_2O$: Al_2O_3 : 6.2 SiO_2 : H_2O
Crystal size and Habit: spherical aggregates (1 to 10μm) of submicron crystals (< 0.1 to 0.2 μm)[b]

References

[1] D. E. W. Vaughan, K. G. Strohmaier, U. S. Patent 5 013 536 (1991)
[2] D. E. W. Vaughan, K. G. Strohmaier, Micropor. Mesopor. Mater. 28 (1999) 233

Notes

a. Both 12 and 16 day samples were excellent PAU.
b. ^{13}C-NMR shows two sites; ^{29}Si-NMR shows three broad peaks.

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PAU — Paulingite (seeded) — Si(76), Al(24)

Contributed by David Vaughan and Karl Strohmaier

Verified by P. Piccione and by B. Subotic´

Type Material: $(Na_{87}K_{72}TEA_{15})[Al_{164}Si_{508}O_{1344}] : wH_2O$ (TEA = tetraethylammonium)

Method: D. E. W. Vaughan, K. G. Strohmaier [1,2]

Batch Composition: $0.5\ K_2O : 0.7\ Na_2O : 1.3\ (TEA)_2O : Al_2O_3 : 9\ SiO_2 : 0.4\ Na_2SO_4 : 135\ H_2O$

Source Materials

deionized water
sodium hydroxide (J.T. Baker, ~99% NaOH)
alumina (Alcoa C-31, >99% $Al_2O_3 \cdot 3\ H_2O$)
sodium silicate (PQ Corp. N-brand, 8.9% Na_2O, 28.7% SiO_2)
potassium hydroxide (J. T. Baker, >99% $KOH \cdot 0.5\ H_2O$)
silica sol (Dupont HS-40, 40% SiO_2, 0.4% Na_2O)
tetraethylammonium hydroxide (RSA Corp., 40% $N(C_2H_5)_4OH$)
aluminum sulfate (> 99% $Al_2(SO_4)_3 \cdot 17\ H_2O$)

Batch Preparation (for 17 g dry product)

Preparation of Seed Solution [3,4]

(1) [30 g water + 16 g NaOH + 3.25 g alumina] reflux until a clear solution forms, then cool to room temperature and add water back to the original weight if necessary
(2) [54.4 g sodium silicate + 31.3 g water + (1)], add sodium aluminate solution slowly with mixing in a 200 mL Waring blender
(3) Age for 24 hours at room temperature[a]

Preparation of Crystallization Batch

(4) [6 g water + 2.28 g potassium hydroxide + 2.16 g sodium hydroxide + 4.57 g alumina], stir at 100°C until clear, then cool in an ice bath to below room temperature. Adjust to original weight with water
(5) [45.9 g silica sol + 4.53 g seed solution + 33.4 g tetraethylammonium hydroxide + (4)], add sequentially with continuous mixing
(6) [6 g water + 3.2 g aluminum sulfate], mix until dissolved
(7) [(5) + (6)], add alum solution slowly with continuous mixing
(8) [(7) + 17 g water], adjust the total weight of gel to 125 g by the addition of water[b]

Crystallization

vessel: 125 mL Teflon jar or bottle (Nalgene)
time: 22 days
temperature: 100°C
agitation: none

Product Recovery

(1) Vacuum filter on a Buechner funnel
(2) Wash to pH < 10
(3) Dry at 110°C
(4) Yield: 17 g (~85% on Al_2O_3)

PrimeBooks

Product Characterization

XRD: excellent PAU

Elemental analyses: 0.44 K_2O : 0.53 Na_2O : 0.09 $(TEA)_2O$: Al_2O_3 : 6.18 SiO_2

Crystal size and habit: spherical aggregates (2 to 30 μm) of submicron crystals (0.1 to 0.3 μm)[c]

References

[1] D. E. W. Vaughan, K. G. Strohmaier, US Patent 5 013 536 (1991)
[2] D. E. W. Vaughan, K. G. Strohmaier, Micropor. Mesopor. Mater. 28 (1999) 233
[3] D. E. W. Vaughan, U S Patent 4 178 352
[4] D. E. W. Vaughan, Mater. Res. Soc. Symp. Proc. 111 (1988) 89

Notes

a. Stored at room temperature, this seed solution will be stable and usable for several months.

b. The control of OH^-/Si ratios can be done either by adding part of the Al as aluminum sulfate, or by using only aluminate and balancing the alkalinity with mineral acid (such as sulfuric acid).

c. ^{13}C-NMR shows two sites; ^{29}Si-NMR shows three broad peaks.

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PHI — Phillipsite — Si(72), Al(28)

Contributed by David Hayhurst

Verified by A. Cichocki, by A. Rodriguez, by E. Falabella Sousa-Aguiar, and by R. Thompson and A. Giaya

Type Material: $K_{3.1}Na_{0.9}[Al_4Si_{12}O_{32}] : wH_2O$

Method: D. T. Hayhurst, L. B. Sand [1]

Batch Composition: 6.95 Na_2O : 3.50 K_2O : Al_2O_3 : 18.5 SiO_2 : 325 H_2O

Source Materials

distilled water
potassium hydroxide (Mallinckrodt reagent grade, 87% KOH)
sodium silicate solution (PQ Corp., N-brand, 8.9% Na_2O, 28.7% SiO_2)
sodium aluminate (Nalco, 30.5% Na_2O, 45.6% Al_2O_3)

Batch Preparation (for 100 g dry product)

(1) [636 g water + 91.6 g potassium hydroxide + 826.9 g sodium silicate solution]. Dissolve in a stirred flask at 100°C under reflux
(2) [(1) + 45.28 g sodium aluminate], continue mixing at 100°C for crystallization

DropBooks

Crystallization

Vessel: 3 L, 3-neck flask under reflux
Temperature: 100°C
Time: 6 to 8 hours
Agitation: mechanically stirred

Product Recovery

(1) Filter to recover solids
(2) Wash to pH < 10
(3) Dry at 120°C
(4) Yield: 100% on Al_2O_3

Product Characterization:

XRD: PHI (only crystalline product); Competing phases; MOR,[a] ERI,[a] LTL,[b] GIS,[b] ANA[c]
Elemental Analysis: 0.8 $K_2O \cdot 0.2\ Na_2O \cdot Al_2O_3 \cdot 5.24\ SiO_2$
Crystal Size and Habit: multi-crystalline aggregates, ~5 μm dia.

Reference

[1] D. T. Hayhurst, L. B. Sand, in ACS Symposium Series 40, J. R. Katzer (ed.), Am. Chem. Soc., Washington, D. C., 1977, p. 219

Notes

a. Higher silica batch composition
b. $K^+/(Na^+ + K^+) > 0.4$
c. $K^+/(Na^+ + K^+) < 0.1$

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PHI — High-alumina Phillipsite — Si(67), Al(33)

Contributed by Andrzej Cichocki

Verified by J. Bronic´ and by G. Kühl

Type Material: $Na_{6.3}K_{4.2}[Al_{10.5}Si_{21.5}O_{64}] \cdot 23\ H_2O$[a]

Method: A. Cichocki [1,2]

Batch Composition: 1.53 Na_2O : 0.44 K_2O : Al_2O_3 : 5.0 SiO_2 : 82.7 H_2O

Source Materials
distilled water
sodium hydroxide (reagent grade, 97% NaOH)
potassium hydroxide (reagent grade, 86% KOH)
silica sol (Rudniki Chemical Works, 29.5% SiO_2, 0.22% Na_2O)
sodium aluminate solution (26.6% Al_2O_3, 19.6% Na_2O)[b]

Batch Preparation (for 26 g product)
(1) [36.0 g water + 1.53 g sodium hydroxide + 3.78 g potassium hydroxide], dissolve and cool to room temperature
(2) [67.0 g silica sol + (1), mix in a porcelain mortar and stir for 2 minutes
(3) [(2) + 25.22 g sodium aluminate solution], add sodium aluminate drop by drop to the stirred silicate over a 10 minute period and continue stirring for 20 minutes

Crystallization
Vessel: stainless steel autoclave, 120 cm^3 capacity
Aging: 24 hours at room temperature
Temperature: 100°C
Time: 7 days
Agitation: none

Product Recovery
(1) Cool to room temperature; transfer the reaction mixture to a porcelain mortar and grind
(2) Filter and wash in a Buechner funnel until pH of the filtrate is ~10
(3) Dry at 110°C
(4) Equilibrate in laboratory air for a few days
(5) Yield: 25.8 g (near 100% on Al_2O_3)[c]

Product Characterization
XRD: Pure phillipsite (ZK-19 [3] in ASTM Powder Diffraction File) competing phases: ANA, CHA, ERI, LTL
Elemental Analysis: 0.60 $Na_2O \cdot 0.41\ K_2O \cdot Al_2O_3 \cdot 4.07\ SIO_2 \cdot 4.30\ H_2O$[d]
Crystal Size and Habit: ~0.5 to 3 μm diameter, round twinned polycrystals

References

[1] A. Cichocki, Zeolites 11 (1991) 758
[2] A. Cichocki, PL Patent 161 557 (1993)
[3] G. H. Kuehl, Am. Mineral. 54 (1969) 1607
[4] A. Cichocki, PL Patent 100 912 (1979)
[5] A. Cichocki, J. Grochowski, L. Lebioda, Kristall. Technik 14 (1979) 9
[6] A. Cichocki, PL Patent 162 653 (1993)

Notes

a. Al content of the unit cell varies from 9.5 to 12.8. More siliceous synthetic-type phillipsite forms when (1) higher silica batch composition is used or (2) borosilicate glass corrodes in the alkaline reaction mixture. Phillipsite with $SiO_2/Al_2O_3 = 6.27$ crystallized in a stainless steel autoclave from a reaction mixture of composition 7.16 Na_2O : 2.81 K_2O : Al_2O_3 : 26.5 SiO_2 : 442 H_2O. [4,5] Phillipsite with $SiO_2/Al_2O_3 = 4.34$ forms from a reaction mixture of composition 1.29 Na_2O : 0.37 K_2O : Al_2O_3 : 4.20 SiO_2 : 69.5 H_2O when crystallization is carried out in a borosilicate glass vessel. These compositions differ slightly from those given in reference [4] and [6] where NaOH and KOH were assumed 100%.

b. Prepared by the reaction of aluminum shavings with concentrated sodium hydroxide solution (~30 wt% NaOH).

c. Dry product contains 72.0% of the sum of Na_2O, K_2O, Al_2O_3 and SiO_2 masses introduced into the reaction mixture.

d. Sorptive Capacity (g/g at $p/p_o = 0.2$): 0.185 for H_2O at 298 K, 0.002 for Ar at 77 K.

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RHO — High-silica Rho — Si(80), Al(20)

Contributed by Alain Matijasic and Joël Patarin

Verified by S. Schwarz, by T. Cholley, and by G. Gbery and K. Balkus

Type Material: $Na_{6.8}Cs_{3.0}[Al_{9.8}Si_{38.2}O_{96}] : (18\text{-}C\text{-}6) \cdot wH_2O$ $(w \approx 29)$

Method: T. Chatelain, J. Patarin, E. Fousson, M. Soulard, J. L. Guth, P. Schulz [1]

Batch Composition: $1.8Na_2O : 0.3Cs_2O : Al_2O_3 : 10SiO_2 : 0.5(18\text{-}C\text{-}6) : 100H_2O$

Source Materials

distilled water
18-C-6 (Lancaster, > 98% cycl. $(C_2H_4O)_6$)
cesium hydroxide (Aldrich, 50% CsOH in water)
sodium hydroxide (SDS, > 98% NaOH)
sodium aluminate (Carlo Erba, 56% Al_2O_3, 37% Na_2O,7% H_2O)
silica sol (Dupont Ludox AS-40, 40% SiO_2)

Batch Preparation (for ~6 g product)[a]

(1) [7.84 g water + 1.35 g 18-C-6 + 1.80 g cesium hydroxide solution + 0.59 g sodium hydroxide], stir until dissolved [b]
(2) [(1) + 1.82 g sodium aluminate], stir until homogenized
(3) [(2) + 15.00 g silica sol], stir until homogenized (formation of a gel) Continue stirring with magnetic stirrer for 24 h., then transfer to a PTFE-lined stainless-steel autoclave. Gel pH = 14

Crystallization

Vessel: 120 mL PTFE-lined stainless steel autoclave
Time: 192 hours
Temperature: 110°C in a preheated oven
Agitation: none. Final pH approximately 12

Product Recovery

(1) Dilute the reaction mixture with distilled water
(2) Filter and wash until pH ≈ 10
(3) Dry at 60°C overnight
(4) Yield: ~ 6 g as-synthesized RHO-type sample (product containing about one molecule 18-C-6 as organic template per unit cell)[b]

Product Characterization

XRD: Strong RHO pattern showing cubic symmetry. (a_o=15.031(1)Å);[c] no visible impurities
Elemental Analyses: Si/Al is close to 3.9[b]
Crystal size and habit: The crystals display a sphere-like shape with an average size of 1 μm

Reference

[1] T. Chatelain, J. Patarin, E. Fousson, M. Soulard, J. L. Guth, P. Schulz, Micropor. Mat. 4 (1995) 231

Notes

a. This recipe has been successfully scaled up by a factor of six.
b. The starting mixture is prepared in a polyethylene vessel.
c. According to Ref. [1].

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SOD NaBr-Sodalite Si(50), Al(50)

Contributed by Andreas Stein

Verified by B. Schoeman and by S. Kowalak

Type Material: $Na_6Al_6Si_6O_{24}$: 2 NaBr [a,b]

Method: A. Stein, G. Ozin, G. Stucky [1, 2][c]

Batch Composition: $Al(OH)_3$: SiO_2 : 12.5 NaOH : 7.5 NaBr : 144 H_2O

Source Materials

deionized water
sodium hydroxide (Mallinckrodt, 98.7%)
sodium bromide (Mallinckroft, 99.0%)
silica sol (DuPont Ludox HS-40, 40% SiO_2)
aluminum hydroxide (Fisher, 99.8%)

Batch Preparation (for 34 g dry product)

(1) [300 mL water + 60.0 g sodium hydroxide + 154.3 g sodium bromide], stir until dissolved
(2) [(1) + 30.0 g silica sol], stir rapidly, heat to 95°C
(3) [200 mL water + 40.0 g sodium hydroxide + 15.6 g aluminum hydroxide], stir, heat at 95°C until dissolved
(4) [Add hot (3) with hot (2)], shake gel vigorously for 5 minutes

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Crystallization

Vessel: 1000 mL capped Teflon bottle
Time: 24 hours
Temperature: 95°C
Agitation: none

Product Recovery

(1) Cool to ambient temperature
(2) Filter [d]
(3) Wash with deionized water until filtrate is bromide-free and pH≈7
(4) Dry at 110°C
(5) Yield; close to 100% on silica and alumina

Product Characterization

XRD: SOD, no other crystalline or amorphous material detected
Elemental Analysis: $Na_{7.5}Br_{1.8}(AlSiO_4)_6$ [e]
Crystal Size and Habit: 50-500 nm[f] dodecahedra, some malformed dodecahedra and penetration twins

References

[1] A. Stein, G. A. Ozin, G. Stucky, J. Am. Chem Soc. 114 (1992) 5171
[2] A. Stein, G. Ozin, in Advances in the Synthesis and Reactivity of Solids, Vol. 2, JAI Press, Greenwich, CT, 1994, p. 93
[3] D. J. Schipper, C. Z. van Doorn, P. T. Bolwijn, J. Am. Ceram. Soc. 55 (1972) 256
[4] R. R. Neurgaonkar, F. A. Hummel, Mater. Res. Bull. 11 (1976) 61
[5] I. F. Chang, J. Electrochem. Soc. 121 (1974) 815
[6] S. C. Zilio, V. S. Bagnato, J. Phys. Chem. 88 (1984) 1373

Notes

a. Other anions that can be introduced by various methods include OH^-, Cl^-, Br^-, I^-, CN^-, SCN^-, ClO_3^-, ClO_4^-, BrO_3^-, No_2^-, N_3^-, $B(OH)_4^-$, $Al(OH)_4^-$, HCO_2^-, $CH_3CO_2^-$, $C_2O_4^{2-}$, CO_3^{2-}, S^{2-}, SO_3^{2-}, SO_4^{2-}, MnO_4^-, SeO_4^{2-}, MoO_4^2, TeO_4^{2-}, WO_4^{2-}, PO_4^{3-}, e^-.

b. Synthesis of NaOH-SOD: $Na_6Al_6Si_6O_{24} \cdot 2\ NaOH \cdot 8\ H_2O$: batch $Al(OH)_3 : SiO_2 :$ 5 NaOH : 41 H_2O. [1] Extensive washing, especially with hot water, results in extraction of hydroxide and sodium ions.

c. Other methods for sodalite synthesis include sintering [3, 4] and structure conversion. [5]

d. Alternately: centrifuge for 20 minutes, decant mother liquor, add fresh water and disperse the solid phase by shaking, followed by centrifuging. Repeat six times.

e. Low cation and anion content is due to formation of some OH^- containing cages (or anion-free cages in washing). These can be removed by heating the sodalite with NaBr. [6]

f. The larger crystallites are obtained in more dilute solutions.

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Verified Syntheses of Zeolitic Materials. H. Robson, editor.

STT SSZ-23 Si(100)

Contributed by M. A. Camblor and M. J. Díaz-Cabañas

Verified by S. Zones, and by Y. Kubota and R. Bandyopadhyay

Type Material: $[Si_{64}O_{128}]$

Method: M. A. Camblor, M. J. Díaz-Cabañas, P. A. Cox, I. J. Shannon, P. Lightfoot, P. A. Wright, R. E. Morris [1]

Gel Composition: SiO_2 : 0.51 TMAdaOH : 0.51 HF : 10 H_2O[a]
(TMAdaOH = N,N,N-trimethyl-1-adamantammonium hydroxide)

Source Materials
tetraethylorthosilicate (TEOS), Merck, (> 98%)
N,N,N-trimethyl-1-adamantammonium hydroxide (0.435 mol/1000 g)[b]
hydrofluoric acid (Aldrich, 48% HF)

Gel Preparation (for 5 g product)
(1) [15.60 g TEOS + 86.10 g TMAdaOH (aq. 0.435 mol/1000 g)], stir until ethanol evaporation is completed and until the water is reduced as required to give H_2O/SiO_2 = 10 after addition of HF[c]
(2) [(1) + 1.56 g hydrofluoric acid], stir manually[d]

DropBooks

Crystallization
Vessel: 60 mL stainless steel autoclave with Teflon liner
Time: 11 days
Temperature: 150 ± 2°C
Agitation: autoclaves rotated at 60 rpm

Product Recovery
(1) Quench autoclaves in cold water; final pH ≈ 8
(2) Filter contents; wash the solid with deionized water and dry overnight at 100°C
(3) Yield: 20 g of solid/100 g gel (98% based on SiO_2)

Product Characterization
XRD: STT (no other crystalline phases); competing phases: CHA, SSZ-31[a]
Elemental Analysis (wt%): 1.20 N, 13.50 C, 2.16H, 1.32 F [e,f]
Crystal size and habit: large plate-like twinned crystals; broad crystal-size distribution with crystals up to 30 x 20 x 2 μm

References

[1] M. A. Camblor, M. J. Díaz-Cabañas, P. A. Cox, I. J. Shannon, P. Lightfoot, P. A. Wright, R. E. Morris, submitted to Chem. Mater.
[2] S. I. Zones, Eur. Patent 231 018 (1987)
[3] S. I. Zones, R. A. van Nordstrand, D. S. Santilli, D. M. Wilson, L. Yuen, L. D. Samparia, Stud. Surf. Sci. Catal. 49 (1989) 299

Notes

a. Final gel composition: In the calculation of the final water to silica ratio two things should be taken into account:
(1) Two water molecules per SiO_2 are consumed during the hydrolysis of TEOS and are eliminated from the reaction mixture according to $Si(OEt)_4 + 2\ H_2O \rightarrow SiO_2 + 4\ EtOH\uparrow$
(2) Evaporation of water must be accounted for (see gel preparation). The water to silica ratio has a large effect on the phase selectivity of the crystallization: at low (<6) and high ratios (>15) pure silica CHA and SSZ-31, respectively, crystallize after short heating, although SSZ-23 is the crystallization product after prolonged heating (in the H_2O/SiO_2 range between 3 and 20). At the reported H_2O/SiO_2 ratio of 10, SSZ-23 is the only phase observed between 11 and 45 days of crystallization.

b. Concentration of OH^-: TMAda OH may be prepared by anion exchange of the iodide, which can be obtained by reaction of 1-adamantamine with an excess of methyliodide at room temperature. In a typical synthesis 1-adamantamine (4.667 g) was dissolved in 50 g of chloroform. Then, 11.350 g of $K_2CO_3 \cdot 1.5H_2O$ was added and the mixture was cooled in an ice bath. 13.14 g of CH_3I was then added followed the next day by a second portion of CH_3I (6.5 g). After 7 days, the mixture was filtered and the solid washed with $CHCl_3$. The iodide was converted to the hydroxide by anion exchange with Dowex 1 resin. The yield in the anion exchange of TMAda-I to TMAdaOH is typically >90-95%.

c. Evaporation of ethanol plus water can be monitored by the change in weight. In this example a total weight loss of 76.61 g was necessary. The time needed for this process depends on many factors (total batch weight, size of the vessel, temperature, etc.) and is typically several hours. Complete evaporation of ethanol may be checked by ^1H NMR of the reaction mixture.

d. A white fluid slurry is obtained after addition of HF.

e. Corresponding to $[(TMAda^+)_{4.1}F^-_{3.3}(OH^-)_{0.8}(H_2O)_{1.6}][SiO_2]_{64}$ per unit cell (OH^- is included for electroneutrality and relates to a small concentration of connectivity defects in the as-made material).

f. Al may be introduced into SSZ-23 either in hydroxide medium (as in Ref. [2] and [3]) and, apparently more favorably, in fluoride medium (unpublished results).

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TON ZSM-22 Si(95), Al(05)

Contributed by Günter Kühl

Verified by M. Derewinski and by Y. Oumi

Type Material: $K_{0.1}Al_{0.6}Si_{23.4}O_{48}(DAO)_{0.86}$[a] (DAO = 1,8-diamino-octane)

Method: E. W. Valyocsik [1]

Batch Composition: 8.9 K_2O : Al_2O_3 : 90 SiO_2 : 3 K_2SO_4 : 27.3 DAO : 3588 H_2O

Source Materials

deionized water
aluminum sulfate (99+% $Al_2(SO_4)_3 \cdot 18\ H_2O$)
potassium hydroxide (87.9% KOH)
1,8-diamino-octane (99+%)
silica sol (Dupont AS-30, ammonia stabilized, 30% SiO_2)

Batch Preparation (for 7.5 g dry product)

(1) [18.2 g water + 1.76 g aluminum sulfate], stir until dissolved
(2) [18.2 g water + 4.0 g potassium hydroxide], stir until dissolved
(3) [72.8 g water + 10.4 g 1,8-diamino-octane], stir until dissolved
(4) [26.95 g water + 47.65 g silica sol], mix well
(5) [(1) + (2)], mix well
(6) [(3) + (5)], add (3) to (5); blend
(7) [(4) + (6)], add (4) to (6), stir for 30 minutes[b]

DropBooks

Crystallization

Vessel: stirred autoclave with stainless steel liner
Incubation: 24 hours at room temperature[c]
Temperature: 160°C
Time: 2-3 days
Agitation: vigorous stirring[d]

Product Recovery

(1) Dilute reaction mixture with water
(2) Filter and wash with water
(3) Dry at ambient temperature or at 110°C
(4) Yield: 7.5 g (near 100% on Al_2O_3)

Product Characterization

XRD: TON; competing phase: MEL (trace)[d]
Elemental Analysis: 0.2 K_2O : Al_2O_3 : 39 SiO_2 : 1.44 DAO
Crystal size and habit: needles[e]

Reference

[1] E. W. Valyocsik, US Patent 4 902 406

Notes

a. Missing cations assumed to be protonated DAO.
b. Reaction mixture becomes cloudy but does not gel.
c. It is not certain that aging (or seeding) is beneficial.
d. Ref. [1] recommends a stirring rate of 400 rpm; static preparations or slow stirring produce MEL or mixtures of MEL + TON.
e. The size of the crystallites decreases with increasing stirring rate.

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VFI VPI-5 (DPA method) Al(53), P(47)

Contributed by Heyong He and Jacek Klinowski

Verified by A. Karlsson and by W. Schmidt

Type Material: $[Al_{19}P_{17}O_{72}]$: 0.4 DPA : 42 H_2O (DPA = di-*n*-propylamine)

Method: H. He, J. Klinowski [1]

Batch Composition: 1.00 Al_2O_3 : 1.00 P_2O_5 : 40 H_2O : 1.00 DPA[a]

Source materials

distilled water
pseudoboehmite (Catapal B, 68.01 wt% Al_2O_3)
phosphoric acid (Aldrich, 88.30 wt% H_3PO_4)
di-*n*-propylamine (DPA) (Aldrich, > 98% pure)

Batch Preparation (for ~18 g dry product)

(1) [64.60 g water + 15.00 g pseudoboehmite], disperse alumina in water
(2) [(1) + 22.20 g phosphoric acid], stir until homogeneous (for several minutes) and age for 2 hours without stirring
(3) [(2) + 10.11 g di-*n*-propylamine], stir for 2 hours[b]

DropBooks

Crystallization

Vessel: Teflon-lined autoclave
Time: 4 hours
Temperature: 142°C
Agitation: none

Product Recovery

(1) Dilute the reaction mixture with distilled water
(2) After the crystals precipitate, decant the upper layer of liquid and discard. Repeat the operation three times
(3) Filter and wash the crystals with distilled water
(4) Dry in an air oven below 50°C

Product Characterization

XRD: VFI (a_o = 18.9752 Å, c_o = 8.1044 Å, space group $P6_3$); competing phase: $AlPO_4$-11[c]

Elemental Analysis: 0.04 DPA : Al_2O_3 : 0.9 P_2O_5

Crystal Size and Habit: Crystals are spherical and aggregated, ~ 100 μm dia.

Reference

[1] H. He, J. Klinowski, J. Phys. Chem. 98 (1994) 1192

Notes

a. The amount of water quoted includes water in pseudoboehmite (100% - wt% Al_2O_3), phosphoric acid (100% - wt% P_2O_5).
b. After adding DPA, the gel is very viscous. Homogeneous stirring is therefore essential.
c. $AlPO_4$-11 is found when stirring during Batch Preparation (3) is not vigorous enough.

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VFI VPI-5 (TBA method) Al(50), P(50)

Contributed by Heyong He and Jacek Klinowski

Verified by A. Karlsson and by W. Schmidt

Type Material: $[Al_{18}P_{18}O_{72}] : 42\ H_2O$

Method: H. He, J. Klinowski [1]

Batch Composition: $1.00\ Al_2O_3 : 1.00\ P_2O_5 : 50\ H_2O : 1.12$ TBA-OH[a]
(TBA-OH = tetrabutylammonium hydroxide)

Source materials
distilled water
pseudoboehmite (Catapal B, 68.01 wt% Al_2O_3)
phosphoric acid (Aldrich, 88.30 wt% H_3PO_4)
tetrabutylammonium hydroxide (Fluka, 58.08 wt% TBA-OH)

Batch Preparation
(1) [61.63 g water + 15.00 g pseudoboehmite], disperse alumina in water
(2) [(1) + 22.20 g phosphoric acid], stir until homogeneous (for several minutes) and age for 2 hours without stirring
(3) [(2) + 50.04 g tetrabutylammonium hydroxide], stir for 2 hours

Crystallization
Vessel: Teflon-lined autoclave
Time: 20 hours
Temperature: 150°C
Agitation: none

Product Recovery
(1) Dilute the reaction mixture with distilled water
(2) After the crystals precipitate, decant the upper layer of liquid and discard. Repeat the operation three times
(3) Filter and wash the crystals with distilled water
(4) Dry in an air oven below 50°C

Product Characterization
XRD: VFI (a_o = 18.9752 Å, c_o = 8.1044 Å, space group $P6_3$); competing phases: $AlPO_4$-H2 and H3 [2]
Elemental Analysis: $0.006\ TBA^+ : Al_2O_3 : P_2O_5$
Crystal Size and Habit: needle-like and aggregated into bundles, ~ 10 μm dia.

References
[1] H. He, J. Klinowski, J. Phys. Chem. 98 (1994) 1192
[2] F. d'Yvoire, Bull. Soc. Chim. 372 (1961) 1762

Note
a. The amount of water quoted includes water in pseudoboehmite (100% - wt% Al_2O_3), phosphoric acid (100% - wt% P_2O_5), and tetrabutylammonium hydroxide (100% - wt% TBA-OH).

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SUZ-4 Si(86), Al(14)

Contributed by Geoffrey L. Price

Verified by M. Camblor, by P. Piccione, and by E. Creyghton

Type Material: $K_x(TEA)_{5-x}[Al_5Si_{31}O_{72}] \cdot wH_2O$ (TEA = tetraethylammonium)

Method: G. L. Price

Batch Composition 7.35 K_2O : Al_2O_3 : 33.3 SiO_2 : 3.10 $(TEA)_2O$: 681 H_2O

Source Material

distilled, deionized water
potassium hydroxide (Fisher A.C.S. pellets, 86% KOH)
aluminum pellets (Aldrich, 99.99+% Al)
tetraethylammonium hydroxide (Aldrich aqueous solution, 35% TEA-OH)
silica sol (Dupont Ludox AS-40, ammonium stabilized, 40% SiO_2)

Batch Preparation (for 13 g dry product)[a]

(1) [33.98 g water + 6.709 g potassium hydroxide], stir until dissolved
(2) [(1) + 0.3776 aluminum pellets], stir overnight or until Al pellets dissolve completely in a loosely capped plastic bottle (hydrogen gas evolved)
(3) [18.226 g tetraethylammonium hydroxide + 35.00 g silica sol + 29.04 g water]. Stir together
(4) [(2) + (3)], mix well

DropBooks

Crystallization

Vessel: 200 mL stainless steel autoclave
Temperature: 150°C
Time: 4 days
Agitation: rotated autoclave[a]

Product Recovery

(1) Cool to ambient temperature; decant and discard liquid
(2) Wash with water to pH < 10
(3) Dry at 100°C
(4) Yield: near 100% on Al_2O_3

Product Characterization

XRD: strong SUZ-4 [1,2]; competing phases MOR[b] plus an unidentified phase[c]
Elemental analysis: wt% Si 36, Al 5.5, K 1.5
Crystal size and habit: rods, 0.1 mμ dia. x 1 mμ long

References

[1] S. L. Lawton, J. M. Bennett, J. L. Schlenker, M. J. Rubin, J. Chem.Soc.,Chem.Commun.(1993) 894
[2] D. B. Lukyanov, V. L. Zholobenko, J. Dwyer, S. A. I. Barri, W. J. Smith, J. Phys. Chem B 103 (1999) 197

Notes

a. This preparation has been successfully scaled up to a one-liter stirred autoclave.
b. Na^+ level too high.
c. Produced by inadequate agitation during crystallization. XRD lines observed at 14.0°(2θ) m, 22.8° ms, 28.3 s, 29.8° ms, 30.6 m and 40.9 mw.